Chapter 7

Oxidation of NiAl(110) at medium oxygen pressures

During thermally controlled oxidation of NiAl, aluminium oxide is formed and its structural properties, thickness and morphology are strongly dependent on the oxidation conditions. Thin aluminium oxide layers can be grown upon exposure of low-index NiAl surfaces. Their structure and the growth mode is strongly influenced by the substrate orientation: a three-dimensional island growth was reported on the (100) surface [25], whereas well-ordered ultra-thin oxide layers may be grown by oxidation of the (110) surface [7, 8, 9, 25, 102].

We have investigated the ultra-thin aluminum oxide grown on the NiAl(110) and its transition to bulk oxides as a function of the partial oxygen pressure and temperature. The main experimental technique employed for this study is surface x-ray diffraction. In addition, ex situ TEM measurements were performed in order to gain insight on the oxide microstructure and the oxide/substrate interface.

This chapter is organized as follows: section 7.1 gives an overview of the previous findings concerning the structural aspects of the ultra-thin aluminium layer, followed in section 7.2 by the description of the sample preparation procedure and the experimental set-up used for the diffraction experiments. A comparison between our experimental diffraction data and the theoretical model of the ultra-thin aluminium model proposed by Kresse et al. [8] is presented in section 7.3.1. The controversial interfacial structure for the ultra-thin aluminium oxide on NiAl(110) is also discussed in section 7.3.1. The evolution of the ultra-thin oxide layer at 350°C has been followed in situ applying progressively higher oxygen pressures, thus capturing the initial stages of bulk-like oxide growth. These results are presented in section 7.3.3. The oxidation of the clean NiAl(110) surface at 800°C is discussed in the section 7.3.4. The chapter concludes with section 7.4 which comprises the summary of the main experimental observations presented here.
7.1 Introduction

The ultra-thin aluminium oxide layer formed on the (110) surface of NiAl has a highly complex structure and has attracted a lot of scientific interest during the last two decades. The film exhibits a high degree of crystallinity and very good reproducibility in preparation. By dosing 1200 L oxygen at $T=270^\circ$C an amorphous oxide in formed, which crystallizes upon annealing at $T=800^\circ$C [103, 104].

Sustained scientific efforts have been made over the past years in order to solve the structure of the oxide layer. Various experiments, like low energy electron diffraction, electron energy loss spectroscopy (EELS), x-ray photoemission spectroscopy (XPS), angle-resolved ultraviolet photoemission spectroscopy (ARUPS), auger electron spectroscopy, scanning tunneling microscopy (STM) and ion scattering spectroscopy (ISS) have been performed [103, 104]. The most important features proposed on the basis of these investigations are:

- The oxide film is atomically flat and has a layered structure with a thickness of 5 Å. This is compatible with two bilayers consisting each of an aluminium layer and a distorted hexagonal oxygen layer;

- The oxide is commensurate with the substrate along the $[1\bar{1}0]_{\text{NiAl}}$ direction and incommensurate in the $[001]_{\text{NiAl}}$ direction;

- There are two domains of the oxide overlayer which are rotated by 24° with respect to the substrate unit cell;

- The oxide film is oxygen-terminated.

Although some initial studies were pointing to a structure derived from the bulk $\alpha$- or $\gamma$-alumina [103], a detailed atomistic model of the oxide layer was missing for more than two decades. Extended SXRD investigations have been recently performed by Stierle et al. [7] and a structural model has been proposed. It has the Al$_2$O$_3$ stoichiometry and is derived from the $\kappa$-alumina polymorph. The oxide is composed of a double layer of strongly distorted hexagonal arrangement of oxygen ions hosting aluminum ions on both octahedral and tetrahedral sites with equal probability.

Fig. 7.1(a) shows the LEED pattern of the ultra-thin oxide on NiAl(110) recorded at an electron energy of 67 eV. The reciprocal unit cell of the substrate is indicated in the figure. The real space lattice constants were found to be $a=18.01$ Å and $b=10.59$ Å, $\gamma = 91.15^\circ$ and the orientation of the oxide lattice relative to the substrate is shown schematically.
7.1 Introduction

in Fig. 7.1(c). As previously mentioned, the oxide lattice can be rotated by $\pm 24.01^\circ$ with respect to the substrate [110] direction, corresponding to the formation of twin domains.

The in-plane diffraction map of the oxide layer corresponding to only one domain is presented in Fig. 7.1(b). The full and the open half-circles indicate the experimental and the best-fit structure factors, respectively. The red hexagon marks the reflections that arise from the distorted hexagonal structure having a side length of 3 Å. The out-of-plane structure of the oxide was probed by measuring the intensity along the surface rods of the oxide. Fig. 7.2 shows the surface rod scattering for different values of the in-plane momentum transfer as a function of the reciprocal lattice coordinate, $L$. The red curves represent best-fit structure factors for the proposed structural model, which is shown in Fig. 7.3. The light and dark blue spheres represent the oxygen ions located at the surface and interface, respectively, whereas the red and orange spheres indicate the aluminium ions in the topmost and interfacial layer, respectively. The oxygen ion double layer was found to be buckled along the [100] direction of the oxide lattice.

Another structural model has been proposed by Kresse et al. [8] based on STM measurements and DFT calculations. The stoichiometry of this structure was reported to be Al$_{10}$O$_{13}$, in contrast to the bulk Al$_2$O$_3$. The top and side views of the DFT-based structural model are shown in Fig. 7.3.

Figure 7.1: (a) LEED pattern of the ultra-thin oxide layer on NiAl(110). The bulk coordinates of the substrate are indicated [7]. (b) In-plane diffraction data of the oxide layer for one twin domain. The size of the half circles is proportional to the structure factor. Full half-circles, experimental structure factors; open half circles, best-fit structure factors. The red hexagon indicates the reflections that arise from a distorted hexagonal structure with a side length of 3 Å. The dashed circle denotes the reciprocal space area displayed in the LEED pattern in (a) [7]. (c) Orientation relations between the NiAl lattice and the oxide film lattice. The oxide lattice can be rotated by $\pm 24.01^\circ$ with respect to the [110] direction, corresponding to the formation of twin domains [7].
Figure 7.2: Experimental x-ray diffraction structure factors (black symbols) as a function of the reciprocal lattice coordinate, $L$, for different in-plane momentum transfers. The red curves represent best-fit structure factors for the proposed structural model. In the inset, the scattering geometry is pictured [7].

model are shown in Fig. 7.4(a) and (b). The light and dark blue spheres represent the interfacial (Al$_i$) and surface (Al$_s$) aluminium ions, respectively, whereas the red spheres represent the oxygen ions. For modeling the interface, the parallelogram-shaped commensurate super-cell indicated in the Fig. 7.4(a) has been adopted. It has twice the area of the conventional oxide unit cell (white rectangle) and the lattice constants are $a=20.67$ Å

Figure 7.3: Top and side view of the best-fit oxide structure. The diagram shows surface oxygen ions (light blue), interfacial oxygen ions (dark blue), Al ions in between the two oxygen ion layers (red), and interfacial Al ions (orange). The oxygen atoms that form rows along the substrate [001] direction are shown in yellow [7].
The topmost oxide layer has the bulk \( \text{Al}_2\text{O}_3 \) stoichiometry and is characterized by an oxygen ion arrangement which can be described in terms of squares and triangles. These are highlighted in Fig. 7.4(a) and (c) (green lines). The aluminum ions are placed in between the oxygens, only slightly below the oxygen layer, as can be observed in Fig. 7.4(f). Additional aluminum ions are present in the oxide layer close to the interface, \( \text{Al}_i \) which are bound strongly to the substrate, thus contributing with only two electrons to the oxide film. The registry to the substrate is enforced by the interfacial \( \text{Al}_i \) atoms which are mostly sitting above the Ni rows. This model was found to be energetically more favorable as compared to the previously described SXRD-model [8].

A comparison between the DFT-based model and our experimental diffraction data will be shown in section 7.3.3.
7.2 Experimental details

Sample preparation

The experiments described in this chapter were performed using a nominally Ni$_{50}$Al$_{50}$ single crystal with the diameter 10 mm and the thickness of 2 mm. The specimen has been cut parallel to the (110) planes and oriented by x-ray diffraction better than 0.1°. It has been polished on one side using alumina particles down to 0.05 µm.

Prior the diffraction experiments, the NiAl(110) sample surface was prepared in the UHV preparation chamber at the MPI laboratory. The substrate has been fixed on a molybdenum sample holder by spot-welding using thin tantalum foil, as can be seen in the inset of Fig. 7.7. The cleanliness and the quality of the sample surface were checked by AES and LEED. Three cycles of Ar$^+$ sputtering (30 minutes at room temperature at 1 keV and $p_{Ar^+}=5\times10^{-6}$ mbar) followed by 5 minutes annealing at 800°C were sufficient to remove the surface contaminants. Fig. 7.5 shows the AES spectrum recorded after the above mentioned cleaning procedure. The specific Auger electron energies for the most common surface contaminants were marked. No signal from either sulphur, carbon or oxygen was detected. In the inset the AES spectrum in the energy region between 38 and 75 eV energy range is shown. The characteristic AES transitions of Ni$^+$ at 60 eV and Al$^+$ at 68 eV are clearly resolved.

The LEED pattern observed after the sputtering and annealing at 800°C showed a (1×1) rectangular net of sharp reflections, indicating a well-ordered surface. In the Fig. 7.6(a) the LEED pattern measured at 91 eV is shown. The white arrows indicate the unit vectors of the substrate reciprocal lattice.

![Figure 7.5: Auger electron spectra recorded for the NiAl(110) after the cleaning procedure.](image)
7.2 Experimental details

Figure 7.6: (a) The LEED pattern from the clean NiAl(110) surface. (b) The LEED pattern of the ultra-thin aluminium oxide on NiAl(110).

An ultra-thin aluminium oxide layer was then grown using the well-established recipe: oxidation at 270°C with $5 \times 10^{-6}$ mbar O$_2$ for 15 minutes followed by 5 minutes annealing at 800°C [7]. In the Fig. 7.6 (b) the LEED pattern of the oxidized NiAl(110) is shown. The energy of the incident electrons was 62 eV. Heating the oxidized sample in vacuum at temperatures around 1000°C leads to the desorption of the ultra-thin oxide film.

After preparation of the well-ordered ultra-thin aluminium oxide layer, the sample was transferred into the portable UHV diffraction chamber, which was then shipped to the synchrotron radiation facility.

Surface x-ray diffraction measurements

The SXRD measurements presented in this chapter have been performed at the beamline ID32 at the European Synchrotron Radiation Facility, Grenoble. The experimental set-up used during the beamtime$^1$ is illustrated in Fig. 7.7. In the inset of Fig. 7.7 the NiAl(110) sample mounted on the inconel sample holder is shown. The oxidation experiments were performed in the portable UHV diffraction chamber described in Chapter 4. In addition, the chamber was equipped with an Ar$^+$ ion sputtering gun which facilitated the preparation of a clean substrate surface whenever needed during the measurements. The temperature was monitored using a Chromel-Alumel thermocouple which was placed close to the heater. A photon energy of 12.5 keV ($\lambda=0.9918$ Å) was chosen to be far away from any adsorption edge of Ni or Al, thus reducing the fluorescent background from the substrate. The measurements were performed in a horizontal scattering geometry (with

$^1$The diffraction data presented in this chapter were obtained during the ESRF1 beamtime.
the sample surface normal vertical). For the quantitative measurements the incident angle was fixed to 0.4°, which is higher than the critical angle for total reflection of NiAl. The horizontal and vertical detector slits were set to 5×5 mm for both the in-plane and out-of-plane measurements. The structure factor amplitudes have been obtained from the integrated intensities using the software package ANA. In all cases, the appropriate correction factors—background subtraction, active area, rod interception, Lorentz and polarization factors—have been included [54].

Orientation matrix for NiAl(110)

A new unit cell defined in terms of surface orientation has been used to index the diffraction data from the NiAl(110) substrate. It offers a convenient representation of the reciprocal lattice in which the scattering vector, $Q$, is expressed in terms of two in-plane coordinates ($H$ and $K$) which give the parallel component of the momentum transfer, $Q_\parallel$, and the third coordinate, $L$, defining the perpendicular momentum transfer, $Q_\perp$.

The real space unit cell of NiAl(110) and its reciprocal lattice are shown in Fig. 3.4 in Chapter 3. The lattice constants are related to the cubic one—$a_c=2.887$ Å—by: $a=c=a_c$ and $b=a_0\sqrt{2}=4.082$ Å and $\alpha=\beta=\gamma=90^\circ$. The magnitude of the reciprocal lattice vectors is thus $a^*=c^*=1.539$ Å$^{-1}$ and $b^*=2.176$ Å$^{-1}$. The correspondence between the real space directions of the surface and the bulk unit cell of NiAl is: [100]$_{\text{surf}} \parallel [1\overline{1}0]_{\text{bulk}}$; [010]$_{\text{surf}} \parallel [001]_{\text{bulk}}$ and [001]$_{\text{surf}} \parallel [110]_{\text{bulk}}$. The (2, 0, 0) and (0, 1, 0) substrate reflections have been
used for defining the NiAl orientation matrix. All the substrate diffraction data presented in this chapter have been indexed according to this unit cell.

**Orientation matrix for the ultra-thin aluminum oxide**

A different coordinate system has been used to index the reflections arising from the ultra-thin aluminium oxide layer. The orientation of the reciprocal oxide lattice with respect to the underlying substrate is shown schematically in Fig. 7.8. Both aluminium oxide twin domains are indicated (continuous and dotted red lines), together with the substrate directions (black lines). The real space oxide unit cell lattice constants are $a=18.01 \, \AA$, $b=10.59 \, \AA$ and $\alpha=\beta=90^\circ$, $\gamma=91.15^\circ$. The reciprocal lattice is thus characterized by $a^*=0.3489 \, \AA^{-1}$, $b^*=0.5934 \, \AA^{-1}$, $c^*=2.176 \, \AA^{-1}$ and $\alpha^*=\beta^*=90^\circ$, $\gamma^*=88.85^\circ$.

**Orientation matrix for $\gamma$-alumina**

A hexagonal unit cell has been chosen to describe the symmetry of the (111) planes of the $\gamma$-Al$_2$O$_3$ cubic unit cell. This unit cell is depicted in Fig. 7.9 and has the $c$ axis perpendicular to the (111) surface. The oxygen ions are represented by the blue spheres and the octahedrally and tetrahedrally coordinated aluminium ions are marked by the red and magenta spheres, respectively. Viewed along the [111] direction, $\gamma$-Al$_2$O$_3$ structure is characterized by an $ABCABC$ close-packed stacking of the oxygen layers with the cations occupying the octahedrally and tetrahedrally coordinated interstitial sites, as can be seen in Fig. 7.9. The intrinsic hexagonal lattice constants are related to the cubic one—$a_0=7.911 \, \AA$ [69]—by: $a=b=a_0/\sqrt{2}$, $a=a_0\sqrt{3}$, with $a=b=5.59 \, \AA$, $c=13.7 \, \AA$ and $\alpha=\beta=90^\circ$, $\gamma=120^\circ$.

![Figure 7.8: Reciprocal space representation of the relative orientation of the ultra-thin aluminium oxide twin domains (red) with respect to the NiAl lattice (black).](image)
7.3 Results and discussion

7.3.1 Ultra-thin aluminium oxide on NiAl(110)

A well-ordered ultra-thin aluminium oxide film was grown by oxidation of NiAl(110) using the recipe described in section 7.2. Structural characterization of both the oxide layer and the interface with the substrate has been performed by means of surface sensitive x-ray diffraction. The experimental findings are discussed in the following sections.

A. Surface oxide structure

A set of 125 in-plane reflections of the ultra-thin oxide film was measured quantitatively by rocking scans at $L=0.03$ and different $H$ and $K$ values ranging from $H=0–12$ and $K=8–8$. The experimental structure factors have been obtained by integration using the software package ANA, including the appropriate correction factors [54].

Fig. 7.10 shows the in-plane map of experimental structure factors (half filled circles) together with those calculated (open half circles) for the DFT-based model proposed by Kresse et al. [8]. The experimental in-plane structure factors are consistent with the data published by Stierle et al. [7], as can be seen by comparison with the in-plane map in Fig. 7.1(c). The in-plane structure factors are reproduced with less accuracy by the DFT-based model, as compared to the SXRD-based model.

A convenient tool to test the in-plane projected structure is offered by the Patterson function, $P(r)$, which is defined as the electron density-density correlation function [52].

Figure 7.9: The hexagonal unit cell of $\gamma$-$\text{Al}_2\text{O}_3$. 

Figure 7.10: In-plane diffraction data for one domain of the ultra-thin aluminium oxide layer. The size of the half circles is proportional to the structure factor. Full half-circles, experimental structure factors; open half-circles, structure factors calculated for the DFT-model proposed in Ref. [8].

For in-plane reflections \((L \sim 0)\) this reduces to

\[
P(x, y) = 2 \sum_{HK} |F_{HK}|^2 \cdot \cos[2\pi(Hx + Ky)],
\]

where \(x, y\) are the atomic coordinates within the unit cell. The strength of the peaks in a contour map of Patterson function is proportional to the product of the electron densities of the atoms that produced that peak. In addition, the positions of the peaks in a Patterson map give information on the sum and the difference between the interatomic vectors corresponding to the investigated surface structure. Fig. 7.11(a) shows the contour map of the Patterson function calculated from the experimental structure factors of the in-plane oxide reflections. The real space unit cell is indicated by the red rectangle. For comparison, the Patterson map of the DFT-based model is shown in Fig. 7.11(b). A detailed visual inspection reveals the presence of some additional peaks in the Patterson map of the calculated model. However, there is an overall satisfactory agreement between the experimental and theoretical map.

Additional information on the out-of-plane structure of the oxide film was obtained by measuring the intensity distribution along the oxide surface rods. The integrated intensities of a total of 92 out-of-plane reflections have been recorded upon rocking the
Figure 7.11: (a) Patterson map from experimental data. (b) Patterson map calculated for the model proposed by Kresse et al. [8].

...sample around its normal. In Fig. 7.12 the experimental structure factor amplitudes (black symbols) of five non-equivalent surface rods are shown. The red curves represent the corresponding structure factors calculated for the DFT-based model.

 Attempts to improve the agreement between the calculated and experimental data have been made by performing a structural refinement using the software ROD [105]. The aluminium and oxygen ions in the oxide were allowed to relax in \(x\), \(y\) and \(z\) directions. Both in-plane and out-of-plane diffraction data (in total, 214 structure factors) have been included for the refinement, but no significant improvement of the fit could be achieved.

B. Interface structure

In general, the selective oxidation of an ordered alloy surface requires a rearrangement of the atoms in substrate surface region, which leads eventually to the formation of point defects. Two different mechanisms have been proposed in the literature for the formation of the ultra-thin aluminium oxide layer on NiAl(110). It was suggested by Jaeger et al. [103] that the 5 Å thick aluminium oxide layer is formed by internal oxidation, i.e., following dissociation, the oxygen penetrate the first two layers of the NiAl substrate forming a disordered layer which crystallizes upon subsequent annealing. Simultaneously, Ni dissolution in the bulk takes place. The second mechanism describes the oxide growth in terms of external oxidation and suggests the segregation of Al atoms to the surface as a key process during the oxide growth. Therefore, if this mechanism is valid, one could eventually expect an enrichment in Al of the first substrate layer(s). It is however not straightforward to discriminate between the different mechanisms based solely on the interfacial structure, since other factors may also be involved (e.g., diffusion is expected to play a role at those temperatures).

Although the issue of the interfacial structure has been already addressed in several
7.3 Results and discussion

Figure 7.12: Experimental structure factors (black symbols) as a function of the reciprocal lattice coordinate, $L$, for different in-plane momentum transfers. For comparison, the structure factors calculated (red curves) from the model proposed in Ref. [8] are shown.

In studies [9, 102], there is still controversy regarding the correct model. In this context, we have performed CTR measurements in order to probe the ultra-thin aluminium oxide/NiAl(110) interface structure. Three independent substrate truncation rods—one superstructure rod, $(0, 1)$ and two fundamental rods, $(2, 0)$ and $(1, 1)$—have been measured. A total of 124 structure factors were obtained by integrating the intensity and applying the appropriate correction factors. The experimental structure factor amplitudes for $(0, 1)$, $(2, 0)$ and $(1, 1)$ crystal truncation rods are represented by the black symbols in...
Fig. 7.13. Experimental structure factor amplitudes (black symbols) for (0, 1), (2, 0) and (1, 1) NiAl crystal truncation rods. The dashed green, the solid red and the dotted blue lines correspond to the structure factors calculated for the interface model I, II, and the DFT-based model, respectively.

In the structural model proposed by Kresse et al. [8], the interface has been modeled using the parallelogram-shaped super-cell—depicted in Fig. 7.4(a)—placed onto 33 NiAl unit cells and the atoms in the first five substrate layers were allowed to relax in $x$, $y$ and $z$-directions. The average, minimum and maximum displacement of both Ni and Al atoms in each layer is listed in the Table 7.1. The displacements are calculated as percents from the NiAl interlayer spacing. The structure factors for (0, 1), (2, 0) and (1, 1) crystal truncation rods have been calculated numerically using ROD and are represented by the dotted blue lines in Fig. 7.13. The poor agreement with the experimental data shows that the proposed model lacks some structural features and can not accurately describe the oxide/alloy interface.

Detailed structure refinement of the interface structure has been performed by fitting all the structure factor amplitudes simultaneously using the software ROD [105]. Two different structural models have been found to describe the observed shape of the truncation rods and will be described below.
I. Al anti-site model The characteristic structural feature of this model is the presence of point defects in the first substrate layer. These are namely, Al anti-site atoms (Al atoms residing on the Ni lattice) and a very low percent of Al vacancies. In addition to these structural defects, the substrate atoms in the first two layers were allowed to relax along the $z$-direction. Nine free parameters were considered for the fit: one overall scale factor, three occupancy parameters and five displacement parameters. Fig. 7.13 shows the experimental structure factors (black symbols) together with those calculated for the best-fit model (full red curves). The fit parameters are listed in Tab. 7.2. There are 84% of Ni regular atoms in the first substrate layer, the rest of Ni sites, namely 16%, being occupied by Al atoms. In turn, the occupancy probability of Al sites in the same layer is 94%. There is a pronounced outward

\[\text{Table 7.1: Displacements of the atoms in the first five substrate layers according to the DFT-based model [8].}\]

<table>
<thead>
<tr>
<th>Layer</th>
<th>Al</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta z$</td>
<td>$\Delta y$</td>
</tr>
<tr>
<td>1st</td>
<td>Mean</td>
<td>-0.88</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>-6.90</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>3.52</td>
</tr>
<tr>
<td>2nd</td>
<td>Mean</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>-3.36</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>2.60</td>
</tr>
<tr>
<td>3rd</td>
<td>Mean</td>
<td>-0.19</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>-1.87</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>0.93</td>
</tr>
<tr>
<td>4th</td>
<td>Mean</td>
<td>-0.20</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>-1.56</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>0.52</td>
</tr>
<tr>
<td>5th</td>
<td>Mean</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>-0.52</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Table 7.2: Site occupancies and displacement parameters obtained for the best-fit model assuming the presence of Al anti-site atoms.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Atom</th>
<th>Occupancy</th>
<th>$\Delta z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st layer</td>
<td>Al</td>
<td>0.94</td>
<td>-2.78%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>0.84</td>
<td>-3.16%</td>
</tr>
<tr>
<td></td>
<td>Al AS</td>
<td>0.16</td>
<td>+68%</td>
</tr>
<tr>
<td>2nd layer</td>
<td>Al</td>
<td>1.00</td>
<td>+1.4%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>1.00</td>
<td>-2.2%</td>
</tr>
</tbody>
</table>

Displacement of the Al anti-site atoms (68%, if expressed in terms of NiAl interlayer spacing), while both the regular Ni and Al atoms in the first layer are slightly displaced inwards. This means effectively that the Al anti-site atoms are in fact closer to the oxide layer than the substrate. The second substrate layer maintains the bulk stoichiometry and small inward and outwards displacements were found for the Ni and Al atoms, respectively. It is important to emphasize that this model is consistent with the one previously proposed by Stierle et al. [9]: 18% of Al anti-site atoms showing significant outward displacements were reported to be present in the first substrate layer. In addition, there are 5% of Ni anti-site atoms in the second substrate layer. It was argued that the destructive interference close to the anti-Bragg point ($L=1$) on the $(0,1)$ superstructure rod can be considered as a signature for the presence of interfacial Al anti-site atoms, which are stabilized at the interface by the presence of the aluminium oxide layer; their pronounced outward displacement could be understood in terms of a strong interaction of Al anti-site atoms with the oxide overlayer. However, according to the Ni-Al phase diagram, these defects are forbidden in the bulk $\beta$-NiAl and Ni vacancies are expected to form on the Al-rich side [see section 5.1 in Chapter 5].

II. Displacement model Recent theoretical studies [8] have suggested that the presence of Al anti-site atoms at this interface is energetically very costly. A model which assumes a perfect bulk stoichiometry and only displacements of the atoms in the first few substrate layers is considered to be energetically more favorable. This would imply that during the formation of the aluminium oxide, a vertical mass transport of aluminium and nickel atoms sets in to cancel out the concentration gradient which appears due to selective oxidation of the substrate. Therefore, an interfacial model based solely on vertical displacements of the atoms residing in the first three
7.3 Results and discussion

<table>
<thead>
<tr>
<th>Layer</th>
<th>Atom</th>
<th>Occupancy</th>
<th>Δz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st} layer</td>
<td>Al</td>
<td>1.00</td>
<td>-2.38%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>1.00</td>
<td>-2.46%</td>
</tr>
<tr>
<td>2\textsuperscript{nd} layer</td>
<td>Al</td>
<td>1.00</td>
<td>-1.5%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>1.00</td>
<td>+1.36%</td>
</tr>
<tr>
<td>3\textsuperscript{rd} layer</td>
<td>Al</td>
<td>1.00</td>
<td>-0.74%</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>1.00</td>
<td>+1.16%</td>
</tr>
</tbody>
</table>

substrate layers was considered. Structural refinement\textsuperscript{3} was performed by fitting simultaneously the three truncation rods shown in Fig. 7.13. We have used seven fit parameters, namely the scale factor and six displacement parameters corresponding to the Ni and Al atoms in the first three layers. The best-fit structure factors are represented as dashed green lines in Fig. 7.13. The fit parameters corresponding to this model are listed in Tab. 7.3. The displacements are expressed in terms of NiAl(110) interlayer spacing, $a/2=2.041$ Å. According to the proposed structural model, all the atoms in the first substrate layer are displaced inwards, whereas in the second and the third layers, the Al and Ni atoms are displaced inwards and outwards, respectively.

It is evident from the Fig. 7.13 that a slightly better fit was obtained for the anti-site model. However, this is predicted to be energetically less stable than the displacement-based model \[8\]. As previously mentioned, the model proposed in Ref. \[8\] contains at the interface Al ions in the oxide sitting directly above the Ni atoms in the substrate. An attempt to reconcile the theoretical predictions with the experimental observations has been made by considering a starting model in which six Ni atoms in the topmost substrate located below Al ions have been removed. Structural refinement has been performed allowing $z$-displacements of six Al atoms (previously sitting on top of the removed Ni atoms). Also, vertical relaxations of the Ni and Al atoms in the first two substrate layers were allowed. However, the resulting model did not reproduced the experimentally observed surface rods of the oxide.

In this context, relying solely on the existing experimental evidence, the unambiguous discrimination between these two models is still a critical issue. Anomalous scattering

\textsuperscript{3}The interface was modeled using the parallelogram-shaped super-cell shown in Fig. 7.4(a); the oxide layer was placed onto 33 NiAl unit cells.
measurements at the K adsorption edge of Ni are expected to provide valuable information which will enable one to clearly distinguish between the two aforementioned models. (The atoms having an absorption edge at or just above the incident energy absorb strongly the radiation, which causes a change in the atomic form factors for these atoms. In this situation, the dispersion corrections need to be considered).

7.3.2 Multiple oxidation

Motivated by the requirements for practical applications, attempts have been made to increase the thickness of the well-ordered aluminium oxide layer, while preserving its homogeneity and crystallinity. Various procedures have been suggested in the literature [106, 107, 108]. Among these, it was reported by Yoshitake et al. [106] that the thickness of the ultra-thin aluminum oxide film on NiAl(110) can be increased by performing multiple-oxidation cycles. The results were obtained by means of AES and LEED investigations. The thickness of the oxide layer was estimated based on the O KLL (503 eV) / Ni LMM (848 eV) Auger peak intensity ratio, whose value as a function of oxidation cycle is plotted in Fig. 7.14. The average oxide thickness after nine oxidation cycles was reported to be 1.3 nm.

We have applied the above-mentioned procedure and verified the thickening of the oxide layer by means of crystal truncation rod measurements. As discussed previously, CTRs offer a very sensitive test for probing surface/interface structures, i.e., any change in the structure or chemical order at the interface will lead to a change in intensity measured at the zone boundary (e.g. $L=1$) on the (0,1) superstructure rod of the substrate.

![Image](https://example.com/figure7.14.png)

**Figure 7.14:** Auger intensity ratio of O KLL (503 eV) to Ni LMM (848 eV) is plotted as a function of oxidation cycles [106].
Therefore, an ultra-thin oxide layer has been prepared on NiAl(110) according to the well-established recipe: oxidation at $5 \times 10^{-6}$ mbar O$_2$ and 270°C for 15 minutes, followed by 5 minutes annealing at 800°C. The intensity at the (0,1,0.8) substrate peak was followed in situ during the second oxidation cycle. No change in intensity was observed after 15 minutes of oxygen exposure at $5 \times 10^{-6}$ mbar O$_2$ and 270°C, as can be observed in Fig. 7.15, where the intensity evolution as a function of time is plotted. An unaltered interfacial structure points to the fact that no additional mass transport through the interface took place during the second oxidation cycle. Since any further oxidation can not proceed without mass transport, our results give clear evidence that no thickening of the oxide layer takes place by repeating the above-mentioned oxidation procedure.

In the view of these findings, we suggest that the increase of the O KLL (503 eV) / Ni LMM (848 eV) Auger peak intensity ratio reported in Ref. [106] could be attributed to an increased oxide coverage as a function of oxidation cycles, rather than to oxide thickening. This observation is supported also by Low Energy Electron Microscopy (LEEM) studies [109], which show that even if a relatively uniform film is obtained after the initial oxidation cycle, pinholes revealing the clean NiAl surface reappear after the annealing step when crystallization of the amorphous oxide takes place. The prolonged annealing time (1–2 hours at 800°C in vacuum) used in the oxidation experiments reported in Ref. [106] might cause this effect to be even more dramatic, thus leading to larger areas of oxide-free regions, whose oxidation will then lead to a change in the O/Ni peak intensity ratio in the Auger measurements.
7.3.3 Transition of the ultra-thin aluminium oxide to bulk Al$_2$O$_3$

The ultra-thin aluminium oxide film is a metastable state in which the system is held by energy barriers. Thus, for a certain temperature, there will be a particular oxygen partial pressure for which the mass transport through the oxide layer will be activated and the oxide growth will proceed further. The question of how and under which conditions this transition takes place has been addressed in this work by investigating in situ the stability of the ultra-thin aluminium oxide layer as a function of the oxygen partial pressure at 350°C.

In the first step, an ultra-thin aluminium oxide layer was prepared, then the sample was heated to 350°C and subsequently exposed at progressively higher oxygen pressures, starting with $5\times10^{-6}$ mbar O$_2$. The evolution of the oxide layer and of the interfacial structure was monitored in situ by performing rocking scans on the oxide (0, 4, 0.03) and the substrate (0, 1, 0.8) reflections, respectively. If no change was observed, the oxygen was first pumped off and a higher oxygen pressure was applied. The ultra-thin oxide layer was found to be stable up to a partial oxygen pressure of 0.01 mbar. The sample was then annealed for two hours at 800°C in order to crystallize the newly formed oxide. The evolution of the FWHM and the integrated intensity of both the (0, 4, 0.03) oxide and the (0, 1, 0.8) substrate reflections as a function of p$_{O_2}$ is shown in Fig. 7.16(a). The filled and open circles indicate the substrate and oxide reflections, respectively. In Fig. 7.16(b) and (c) the rocking scans at the above mentioned positions measured at different partial oxygen pressures are plotted. The same symbols and color code as in Fig. 7.16(a) were used: the open and filled symbols represent the oxide and the substrate peak, respectively, and each color indicates a different oxygen pressure which can be read on the $x$-axis of the graph in Fig. 7.16(a). The values plotted in Fig. 7.16(a) were obtained by fitting both the substrate and the oxide peaks shown in Fig. 7.16(b) and (c) by a Gaussian profile. It can be noticed from Fig. 7.16(a) that a decrease in the integrated intensities of the oxide and the substrate reflection took place at $10^{-2}$ mbar oxygen, while the FWHM of both reflections remained unchanged. After increasing the oxygen pressure to 0.2 mbar O$_2$ followed by two hours annealing in vacuum at 800°C, a more significant decrease of the intensity on the oxide peak took place concomitantly with a strong increase in the integrated intensity of the (0, 1, 0.8) substrate peak. In the inset of Fig. 7.16(b) the rocking scan on the (0, 1, 0.8) substrate peak after annealing at 800°C is shown. In addition to the increased intensity, the profile of the peak changes to a Lorentzian, indicative of structural changes in the near surface region of the substrate. A detailed structural characterization of the aluminium oxide/NiAl(110) system has been performed at this stage, with focus both on the interface and the oxide layer structure.
7.3 Results and discussion

Figure 7.16: (a) Evolution of the normalized integrated intensity and the FWHM of the (0, 4, 0.03) oxide peak (open circles) and the (0, 1, 0.8) substrate peak (filled circles) as a function of the partial oxygen pressure during oxidation at 350°C. (b) Rocking scans on (0, 1, 0.8) substrate reflection during oxidation at 350°C and different oxygen pressures. (c) Rocking scans on (0, 4, 0.03) oxide reflection during oxidation at 350°C and different oxygen pressures. [Each color indicates a different oxygen pressure, which can be read on the x-axis of the graph in (a)].
Figure 7.17: Experimental structure factors of the (0, 4) and (6, \bar{2}) oxide surface rods (green symbols) after exposure at 0.2 mbar oxygen and annealing at 800°C. The corresponding structure factors for the ultra-thin oxide layer (black symbols) are shown for comparison. The red curves represent the structure factors calculated from the model proposed in Ref. [8].

A. Ultra-thin aluminium oxide

Fig. 7.17 shows the structure factor amplitude along the (0, 4) and (6, \bar{2}) surface rods (green symbols) measured after oxidation with 0.2 mbar O\textsubscript{2} followed by two hours annealing at 800°C. The corresponding surface rods (black symbols) of the initial ultra-thin oxide layer are also shown for comparison, together with the structure factors calculated for the DFT-based model (red lines). The experimental profiles of the surface rods are very similar, indicating that both the structure and the thickness of the surface oxide are essentially unchanged. However, a decrease of the structure factor amplitude is to be noticed due to a reduced coverage of the substrate with ultra-thin aluminium oxide. Indeed, in addition to the latter, bulk \(\gamma\)-\textsubscript{Al\textsubscript{2}O\textsubscript{3}} islands started to form, as will be discussed further below. Thus, in this experiment we have captured precisely the transition from the ultra-thin oxide layer to the bulk oxide growth. Based on the unchanged profiles of the surface rods, it can be concluded that the ultra-thin oxide doesn’t grow thicker. No intermediate structures were observed and further oxidation proceeds by bulk oxide formation.

B. Epitaxial \(\gamma\)-\textsubscript{Al\textsubscript{2}O\textsubscript{3}}

Under the aforementioned oxidation conditions, \(\gamma\)-alumina formed epitaxially with the (111) plane parallel to the NiAl(110) surface. Both in-plane and out-of-plane diffraction measurements were performed in order to obtain structural information on the newly formed \(\gamma\)-\textsubscript{Al\textsubscript{2}O\textsubscript{3}} oxide. To index the bulk oxide reflections the hexagonal unit cell described in section 7.2 has been used. The in-plane oxide lattice constant was determined experimentally to be \(a=b=5.5\) Å, that is 1.6% smaller than the reported value [69]. The \(H\)
Figure 7.18: Possible in-plane orientation relationships at the fcc(111) / bcc(110) interface.

and $K$ indices describe the in-plane momentum transfer and the $L$ index the perpendicular one, expressed in units of the reciprocal oxide lattice (r.l.u.).

**In-plane structure** Before proceeding to present the in-plane structure of the oxide layer with respect to the substrate, the reader is reminded that the NiAl has the CsCl-structure on a bcc-type of lattice, while the bulk $\gamma$-$\text{Al}_2\text{O}_3$ has a cubic spinel structure with the oxygen ions forming a fcc sublattice. A brief description of the possible structural arrangements at this particular type of interface is given below.

The main in-plane orientation relationships predicted for the fcc(111)/bcc(110) interface are: Nishiyama-Wassermann (NW) [110, 111], Kurdjumov-Sachs (KS) [112] and the $R30^\circ$ [113] orientation. The schematic real space representation for each of these orientations is depicted in Fig. 7.18. The blue spheres represent the oxygen ions in $\gamma$-$\text{Al}_2\text{O}_3$, whereas red and green spheres indicate Al and Ni atoms in the substrate, respectively.

**Nishiyama-Wassermann** For the NW relationship, the [1$\bar{1}$0] direction of the fcc lattice is parallel to the [001]$_{\text{bcc}}$ direction. One can define an angle $\theta$ such that $\theta=0$ when [1$\bar{1}$0]$_{\text{fcc}}$ $\parallel$ [001]$_{\text{bcc}}$.

**Kurdjumov-Sachs** For the KS orientation relationship there are two domains having $\theta=\pm5.26^\circ$ and [1$\bar{1}$0]$_{\text{fcc}}$ $\parallel$ [1$\bar{1}$1]$_{\text{bcc}}$.

**R30°** The third possible orientation relationship is R30° in which [2$\bar{1}$1]$_{\text{fcc}}$ $\parallel$ [001]$_{\text{bcc}}$ and $\theta=30^\circ$. 
Figure 7.19: (a) Diffracted intensity as a function of the in-plane rotation angle, $\theta$, with the scattering angle fixed on the $(2,2,0)$ reflection of $\gamma$-Al$_2$O$_3$. (b) In-plane view of the reciprocal space of the NiAl(110)/$\gamma$-Al$_2$O$_3$(111) interface having a KS orientation relationship. The reciprocal unit cells of NiAl(110) and $\gamma$-Al$_2$O$_3$(111) are represented: black open circles indicate the substrate reflections; the dark and light blue filled circles mark the $\gamma$-alumina reflections.

Fig. 7.19(a) shows the diffracted intensity as a function of the azimuthal angle, $\theta$ (rotation of the sample around its surface normal) for the in-plane momentum transfer $Q=4.56$ Å$^{-1}$, which corresponds to the $(2,2,0)$-type reflections of $\gamma$-Al$_2$O$_3$(111). The observed in-plane reciprocal map of the NiAl(110)/$\gamma$-Al$_2$O$_3$(111) interface is schematically shown in Fig. 7.19(b). The reciprocal unit cells of NiAl(110) and $\gamma$-Al$_2$O$_3$(111) are represented: black open circles indicate the substrate reflections; the dark and light blue filled circles mark the $\gamma$-alumina reflections. The characteristic pattern of the Kurdjumov-Sachs orientation relationship could be identified: there are two $\gamma$-Al$_2$O$_3$ domains which are rotated by $\pm 5^\circ$ with respect to the $(100)$ direction of the substrate. It is interesting to note that the reciprocal space orientation of the oxygen sublattice in $\gamma$-alumina showing the aforementioned orientation [blue dotted line hexagons in Fig. 7.19(b)] is similar to that exhibited by the $(12,0,0)$-type of planes of the ultra-thin aluminium oxide. The corresponding reflections are indicated by the green full circles in Fig. 7.19(b). They appear at slightly smaller momentum transfer, which implies a contraction of the corresponding lattice planes upon transformation to bulk $\gamma$-Al$_2$O$_3$. In conclusion, the relative orientation relationship at the $\gamma$-Al$_2$O$_3$(111)/NiAl(110) interface was determined to be the Kurdjumov-Sachs (KS) orientation [112].

**Out-of-plane structure** The structure of $\gamma$-Al$_2$O$_3$(111) layer was further investigated by performing out-of-plane measurements along the oxide rods, for which an additional
momentum transfer is provided perpendicular to the surface. From bulk structure factor considerations only reflections at \( L = 4 \) and 10 are expected for both \((0, 2, L)\) and \((2, 0, L)\) directions, as can be observed in the left panel of Fig. 7.20. The presence of reflections at \( L = 8 \) indicate the formation of twin domains, which occur where an \( ABC \) stacking sequence of the oxygen layers is reversed to \( CBA \), resulting in \( ABCABCBA \) stacking sequence. A reversed stacking of the oxygen ion layers from \( ABC \) to \( CBA \) corresponds to a 180° rotation of the reciprocal \((H0L)\) plane of \( \gamma\text{-Al}_2\text{O}_3 \) (middle panel in Fig. 7.20. By this rotation, another reciprocal lattice is obtained: along the \((0, 0, L)\) and \((3, 0, L)\) directions there is an overlap of the reflections arising from the above mentioned twin domains (grey circles), while along the \((1, 0, L)\), \((2, 0, L)\), \((4, 0, L)\) directions the two domains contribute at different positions. The reflections arising from the \( ABC \) and \( CBA \) twin domains are indicated by the black and light grey circles, respectively, whereas those for which both domains are contributing are marked by the dark grey circles. Whenever both the \( ABC \) and \( CBA \) stacking of the oxygen ion layers are present, in addition to the \((2, 0, 4)\) and \((2, 0, 10)\) reflections corresponding to the \( ABC \) stacking there are also reflections at \( L = 2 \) and 8 due to the reversed \( CBA \) stacking. This observations make this plane sensitive to the stacking and twin faults in the subsequent \( ABCABC \) layers of oxygen sublattice.

In Fig. 7.21(a) three out-of-plane scans as a function of the \( \gamma\text{-Al}_2\text{O}_3 \) reciprocal lattice coordinate, \( L \), are shown. \( L = 1 \) corresponds to the reciprocal lattice unit of the oxide \(|c^*| = 2\pi/c = 0.4663 \text{ Å}^{-1}\). The presence of both \( ABC \) and \( CBA \) oxide domains could be identified. Due to the KS orientation relationship, there is a superposition of substrate Bragg reflections along certain out-of-plane reciprocal space direction, as can be seen in Fig. 7.21(b). Therefore, additional peaks at non-integer \( L \) values can be observed on the oxide rods. In Fig. 7.21(a), the peaks were marked by arrows and labeled with the corresponding index of the substrate reflections. The FWHM of the \((2, 0, 4)\) and \((2, 0, 8)\) oxide peaks were found to be \( \Delta L = 0.66 \) and 0.84 r.l.u., respectively. The average film
thickness was thus be estimated to be 20 and 16 Å, respectively. No finite film thickness oscillations were observed indicating a broad distribution of oxide island thicknesses.

C. Interface structure

Two independent in-plane momentum transfers have been probed in order to obtain quantitative information on the interfacial structure. The integrated intensity along the (0, 1) and (2, 0) NiAl crystal truncation rods was measured and the structure factors were obtained by integration and applying the suitable correction factors using the program package ANA. In Fig. 7.22 the structure factors along the (0, 1) and (2, 0) NiAl crystal truncation rods are shown (black symbols).

A simple visual inspection indicates a drastic change of the (0, 1) superstructure rod profile as compared to the profile measured after the ultra-thin oxide layer formation (Fig. 7.13, black symbols). However, no significant change was observed for the profile of the (2, 0) fundamental rod. Recalling the discussion on the different origin of fundamental and superstructure rods [see Chapter 2 for details], it is clear that the fundamental rods are not sensitive to the chemical ordering, only to the mean value of the atomic form

\[ 4 \text{The (2,0,4) and (2,0,8) oxide peaks are sensitive only to the ABC and CBA stacking, respectively.} \]
factor per layer, $\bar{f}$. In the particular case of NiAl, one can express this quantity as:

$$\bar{f}_{\text{Al}} = \theta_{\text{Al}}^\text{Al} f_{\text{Al}} + \theta_{\text{Al}}^\text{Ni} f_{\text{Ni}},$$

$$\bar{f}_{\text{Ni}} = \theta_{\text{Ni}}^\text{Ni} f_{\text{Ni}} + \theta_{\text{Ni}}^\text{Al} f_{\text{Al}},$$

where $\theta_{\text{Al}}^\text{Al}$ and $\theta_{\text{Al}}^\text{Ni}$ represent the occupancies of regular Al and Ni sites, respectively, and $\theta_{\text{Ni}}^\text{Ni}$ and $\theta_{\text{Ni}}^\text{Al}$ indicate the occupancies of anti-site Al and Ni atoms, respectively. Thus, the shape of the (2, 0) fundamental rod would remain essentially unchanged as long as the quantity $\bar{f}_{\text{Ni}} + \bar{f}_{\text{Al}}$ is similar to the $f_{\text{Ni}} + f_{\text{Al}}$. On the other hand, an increase of the intensity measured at the anti-Bragg point of a superstructure rod is to be observed when $\bar{f}_{\text{Ni}} - \bar{f}_{\text{Al}} \neq f_{\text{Ni}} - f_{\text{Al}}$. In the following it will be shown that the observed modulation on the (0, 1) superstructure rod of oxidized NiAl is related to the presence of point defects in the topmost substrate layers.

Figure 7.22: Experimental structure factors (black symbols) of the (a) (0, 1) and (b) (2, 0) NiAl CTRs after oxidation at 350°C and annealing at 800°C. The structure factors calculated for the best-fit interface model are indicated by the full red curves [see text for details].

A simultaneous fit of the (0, 1) and (2, 0) rods was performed using the program package ROD [105]. Several free parameters were included, namely, an overall scaling factor, displacement parameters corresponding to relaxations in $z$-direction of the atoms in the first three substrate layers and variable site occupancies for the sites in the first two substrate layers. The structure factors given by the best-fit model are indicated by the full red lines in Fig. 7.22. The model considers the presence of Ni anti-site atoms which occur with 69% and 58% probability in the first two substrate layers. There are also Ni and the Al vacancies in both substrate layers. The occupancy probability for different sites and the average atomic form factor per layer are listed in the Tab. 7.4. In addition, $z$-displacements of the atoms in the first three substrate layers were considered for the structural refinement.
The best-fit structural model for the aluminium oxide/NiAl(110) interface is shown schematically in Fig. 7.23. The displacements for each type of atom are indicated in the figure. They are calculated as percents from the interlayer spacing, 2.0414 Å. The outward relaxation of the Al atoms in the topmost substrate layer amounts 11%, while the Ni and the Ni anti-site atoms show only 3% and 4% displacements, respectively.

To separate the effect of the occupancies and displacements on the rods profile, the structure factor has been calculated numerically by considering in turn only the displacements and the occupancy parameters listed above. The rods profiles are indicated in Fig. 7.22 by the green dotted curve (only z-relaxations) and the blue dotted curve (only occupancies). It can be noticed that the observed modulation is reproduced qualitatively even if one does not include any z-displacement of the atoms. In addition, it should be

<table>
<thead>
<tr>
<th>Layer</th>
<th>$\theta_{\text{Ni}}^{\text{Ni}}$</th>
<th>$\theta_{\text{Al}}^{\text{Al}}$</th>
<th>$\theta_{\text{Ni}}^{\text{Al}}$</th>
<th>$\theta_{\text{Al}}^{\text{Ni}}$</th>
<th>$\bar{f}<em>{\text{Ni}} + \bar{f}</em>{\text{Al}}$</th>
<th>$\bar{f}<em>{\text{Ni}} - \bar{f}</em>{\text{Al}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st layer</td>
<td>0.889</td>
<td>0.105</td>
<td>0.695</td>
<td>0.105</td>
<td>45.715</td>
<td>4.085</td>
</tr>
<tr>
<td>2nd layer</td>
<td>0.7587</td>
<td>0.218</td>
<td>0.576</td>
<td>0.218</td>
<td>40.21</td>
<td>2.36</td>
</tr>
</tbody>
</table>

*Table 7.4:* The occupancy of different sites for the best-fit structural model of the aluminium oxide/NiAl(110) interface [see text for details].

*Figure 7.23:* Structural model of the aluminium oxide/NiAl(110) interface [oxide layer not shown].
7.3 Results and discussion

mentioned that no reasonable fit could be obtained by including only z-displacements as free fit parameters. This increases our confidence that the model gives a realistic description of the interface structure.

The Ni anti-site atoms are reported as the common structural defect which appear on the Ni-rich side of NiAl phase diagram [see Chapter 4]. The Ni enrichment at the interface appears as a consequence of Al consumption by selective oxidation. A recent ab initio thermodynamics study [10] on the structural stability of the Al$_2$O$_3$/ NiAl(110) interface predicts the formation of two types of stable structures depending on the alloy composition. For aluminium oxide being in contact with a Ni-rich alloy, the formation of Ni anti-site atoms at the interface has been predicted. Qualitatively, this is in agreement with our experimental observations. However, Feng et al. [10] have indicated the formation of Ni anti-site atoms on only one substrate layer, whereas our model shows Ni enrichment in the first two NiAl layers. The structure factor has been calculated numerically by assuming bulk occupancy for the second substrate layer. The result is shown by the dot-dashed magenta line in Fig. 7.22 and it clearly indicates that the observed modulation on the (0, 1) superstructure rod can not be reproduced by a model assuming only one Ni-enriched substrate layer.

7.3.4 Oxidation at 800°C

The increase of both the oxidation temperature and the partial oxygen pressure induces considerable changes in the structure of the oxide layer. Exposing the clean NiAl(110) surface at 10 mbar oxygen at 800°C for 90 minutes leads to formation of an oxide layer which consists solely of bulk oxides; the coexistence of epitaxial γ-Al$_2$O$_3$ oxide and polycrystalline δ-Al$_2$O$_3$ was observed.

A. Epitaxial γ-Al$_2$O$_3$

In-plane structure  Fig. 7.24(a) shows the diffracted intensity as a function of the azimuthal angle, θ for the in-plane momentum transfer $Q=4.53$ Å$^{-1}$ measured after the oxidation at 800°C (red symbols). The same scan as in the Fig. 7.19(a) is shown for comparison (blue symbols). There are now three peaks corresponding to (2, 2, 0)- type reflections of γ-Al$_2$O$_3$ which appear at different azimuthal angles compared with the previous scan. This can be understood in terms of a coexistence of oxide domains showing two different relative orientations with respect to the substrate: the Nishiyama-Wassermann (NW) [111, 110] and the R30° orientation [113]. The in-plane view of the reciprocal space of the NiAl(110)/γ-Al$_2$O$_3$(111) interface having the above mentioned orientation relationships is shown in Fig. 7.24(c). The represented reciprocal unit cells are NiAl(110) (black
Oxidation of NiAl(110) at medium oxygen pressures

Figure 7.24: (a) Diffracted intensity as a function of the in-plane rotation angle, $\theta$, with the scattering angle fixed on the (2 2 0) reflection of $\gamma$-Al$_2$O$_3$. (b) Rocking scan on the (420) reflection of $\gamma$-Al$_2$O$_3$ ($\theta = 230^\circ$) after oxidation at 800°C. (c) In-plane view of the reciprocal space of the NiAl(110)/$\gamma$-Al$_2$O$_3$(111) interface having the NW (blue filled circles) and the R30° (red filled circles) orientation relationship.

open circles) and $\gamma$-Al$_2$O$_3$(111) having the NW (blue filled circles) and the R30° (red filled circles) orientation relationship. According to this map, the peaks which appear at $\theta = 170^\circ$ and 230° are due to the oxide domains showing a NW orientation, while the peak at $\theta = 200^\circ$ is attributed to R30° orientated domains. A rather large FWHM characterizes the oxide peaks in the rocking scan shown in Fig. 7.24(a), indicative of a large degree of in-plane misorientation. Fig. 7.24(b) shows the diffracted intensity as a function of the azimuthal angle, $\theta$, with the scattering angle fixed on the (420) reflection of $\gamma$-Al$_2$O$_3$ measured after the oxidation at 800°C. It is basically the oxide peak corresponding to $\theta \sim 230^\circ$ shown in the Fig. 7.24(a) (red line). Three reflections were identified by fitting this peak with a Gaussian lineshape [Fig. 7.24(b)]: the central peak arises from the oxide domains having NW orientation, while the two side peaks correspond to the KS domains. This is indicative of an incomplete transition from KS to NW orientation, whose origin is
explained further below. Based on the rigid lattice model, the KS orientation is expected at the γ-Al₂O₃ (111)/NiAl(110) interfaces as it minimizes the interfacial energy [113]. However, as the film grow thicker the KS domains tend to coalesce in order to decrease the dislocation and defect energy at the domain boundaries. This implies a rotation of the two KS domains by ±5.26° towards each other, a process that was not complete under the investigated oxidation conditions, i.e., 800°C and 10 mbar O₂. The above-mentioned transition was previously observed for the Pdfcc(111)/Crbcc(110) system and the coalescence of the KS domains was investigated as a function of Pd thickness and growth temperature [114].

Out-of-plane structure The out-of-plane structure of the epitaxial oxide was checked by performing L-scans in several reciprocal space directions for both the NW and the R30° oxide domains. These are shown in Fig. 7.25 and correspond to the γ-Al₂O₃ structure [see Fig. 7.20 for comparison]. The presence of (2, 0, 4) and (0, 2, 4) reflections is a signature for twin domains formation. Additional peaks at integer L values appear along (2, 0, L) and (0, 2, L) reciprocal space directions for both NW and R30° domains. They represent contribution from the neighboring oxide rods and are labeled accordingly in the Fig. 7.25.

B. Polycrystalline δ-Al₂O₃

A radial scan performed in a non-high symmetry direction is presented in Fig. 7.26. It reveals the presence of a polycrystalline component which was identified to be δ-Al₂O₃. At oxidation temperatures as high as 800°C and prolonged oxidation times, various metastable alumina phases could form on the NiAl surface. Most often, γ-Al₂O₃ [101, 115] or θ-Al₂O₃ [11] were reported to form on NiAl(110) surface. However, the reflections observed in Fig. 7.26 correspond to those of the tetragonal δ-Al₂O₃ structure reported by Lippens et al. [84].

Careful examination of the diffraction data is required when it comes to discriminate between various transition alumina reflections, since there is a considerable number of common d-spacings. This is illustrated in Fig. 7.26(b) where different d-spacings and momentum transfers characteristic for γ-, θ- and δ-Al₂O₃ reflections are shown. It can be observed that there are a number of δ-Al₂O₃ reflections which might help for an unambiguous interpretation of the experimental data.
Figure 7.25: \(L\)-scans in different reciprocal lattice directions normal to the surface. The reflections were indexed using the coordinates of the hexagonal \(\gamma\)-alumina unit cell. Both the (a) NW and the (b) R30\(^\circ\) domains were probed.

C. Interface structure

Fig. 7.27 shows the structure factor amplitude for the \((0, 1)\) and the \((2, 0)\) substrate truncation rods. While no significant changes in the \((2, 0)\) rod profile, a peak was observed on the \((0, 1)\) superstructure rod. A closer inspection of Fig. 7.24(c) reveals the fact that the \((\bar{1}, 2, L)\) reciprocal space direction of the \(\gamma\)-alumina having the NW orientation relationship overlaps with the \((0, 1)\) superstructure rod of the substrate. Therefore, the peaks at \(L \sim 0.8\) and 1.6 are identified as a contribution from the \((\bar{1}, 2, 3)\) and \((\bar{1}, 2, 6)\) reflections of \(\gamma\)-alumina domains showing the NW orientation, which in turn hampers an atomic level investigation of the interface structure.

D. Ex situ TEM characterization

After the diffraction experiment, cross-sectional TEM specimens were prepared [116] and examined\(^5\) using an in-house JEM-ARM 1250 microscope operated at an accelerating voltage of 1250 kV.

Fig. 8.10(a) shows a conventional transmission electron microscopy image of the alu-

\(^5\)The TEM measurements were performed by Yun Jin-Phillipp, Max-Planck-Institut für Metallforschung, Stuttgart.
7.3 Results and discussion

Figure 7.26: (a) Radial in-plane scan in a non-high symmetry direction after oxidation at 800°C. (b) Comparison between different $d$-spacings characteristic for $\gamma$-, $\theta$- and $\delta$-Al$_2$O$_3$.

Figure 7.27: (a) The structure factor amplitude on the (0, 1) superstructure rod of NiAl. (b) The structure factor amplitude on the (2, 0) fundamental rod of NiAl.

The epitaxial $\gamma$-Al$_2$O$_3$ observed in our study does not form a continuous layer on top of the minimum oxide/NiAl(110) interface. The overall thickness of the oxide layer is estimated to be $\sim$700 Å. In Fig. 8.10(b) a 150 nm wide cavity can be identified at the oxide/alloy interface. The formation of cavities is related to the condensation of vacancies created at the interface as a result of selective oxidation, as perviously explain for the CoGa(100) oxidation [see Chapter 6]. It was reported in the literature [117] that when both transient aluminas and $\alpha$-Al$_2$O$_3$ are present on the surface, the cavities form only underneath the transient phases. This is due to the fact that transient oxides grow mainly by outward Al diffusion through the lattice, which results in an inward diffusion of vacancies to the interface where they reach critical supersaturation level, agglomerate and form voids. On the other hand, $\alpha$-Al$_2$O$_3$ is supposed to grow mainly by inward oxygen diffusion. Therefore, in the regions where the nucleation of the $\alpha$-Al$_2$O$_3$ took place in the early oxidation stages, the amount of injected vacancies is reduced.
Figure 7.28: Cross sectional TEM micrographs showing the $\text{Al}_2\text{O}_3$/NiAl(110) interface.
the substrate. Relatively small oriented domains of $\gamma$-$\text{Al}_2\text{O}_3$ are found to be embedded in a polycrystalline $\delta$-$\text{Al}_2\text{O}_3$ matrix, as can be observed in Fig. 8.10(c). The formation of the polycrystalline oxide is favored by the prolonged oxidation time employed for this experiment (90 minutes). Much shorter exposure times under similar conditions of temperature and pressure (10 mbar O$_2$ at 800°C) are expected to lead to an oxide layer consisting solely of $\gamma$-$\text{Al}_2\text{O}_3$. This idea is supported by the fact that 10 minutes exposure at 870°C and 1 bar O$_2$ leads solely to the growth of an epitaxial $\gamma$-$\text{Al}_2\text{O}_3$, as will be discussed in the Chapter 8.

7.4 Summary

This chapter presented a study of NiAl(110) oxidation at various temperatures and oxygen pressures ranging from $5 \cdot 10^{-6}$ mbar up to 10 mbar O$_2$. Surface x-ray diffraction measurements performed at the synchrotron radiation source ESRF in Grenoble were employed for structural characterization and in situ evolution of the oxide/alloy system during oxidation. Additional information were obtained by means of ex situ TEM investigations. The main results are summarized in the following:

**Ultra-thin aluminium oxide/NiAl(110) interface model**

A set of in-plane reflections and several surface rods corresponding to the ultra-thin aluminium oxide layer have been measured. The DFT-based model proposed by Kresse et al. [8] was found to reproduce reasonably good the surface oxide rods, however structural features were found to be missing in this model for it does not reproduce the observed shape of the crystal truncation rods.

Structural refinement of the interface has been performed and two different models were found to reproduce the experimental data. A better fit was obtained for the Al anti-site model, but this is predicted to be energetically less favorable than the model based solely on relaxation of the atoms in the first three substrate layers. The unambiguous discrimination between these two models is still a critical issue and anomalous scattering measurements at the K adsorption edge of Ni are expected to enable one to clearly distinguish between the two aforementioned models.

**Transition of the ultra-thin aluminium oxide to bulk $\text{Al}_2\text{O}_3$**

We demonstrated that the thickness of the ultrathin aluminium oxide can not be further increased by multiple oxidation cycles and it only exists as a 5 Å thick layer. At 350°C, the surface oxide was found to be stable up to a 0.01 mbar O$_2$. The sample was subsequently annealed at 800°C in order for the newly formed oxide to crystallize. Further oxidation proceeds by the formation of epitaxial bulk $\gamma$-$\text{Al}_2\text{O}_3$ islands having Kurdjumov-Sachs
orientation that coexist with the initial oxide layer.

**Oxidation at 800°C**

γ-Al$_2$O$_3$ oxide islands having both the Nishiyama-Wassermann and R30° in-plane orientation with respect to the substrate formed by oxidation of the NiAl(110) substrate at 800°C and 10 mbar O$_2$. In addition, the presence of polycrystalline δ-Al$_2$O$_3$ was identified. The transition from the KS to NW orientation was previously observed for the Pd(111)/Cr(110) system [114]. As it will be shown in the following chapter, at slightly higher growth temperatures (870°C) and shorter oxidation times (10 minutes), only epitaxial γ-alumina showing a R30° orientation relationship was formed. This is an indication that as the oxide grows thicker, the R30° orientation becomes more favorable. This experimental observation is supported by a recent *ab initio* thermodynamics study [10], which showed that the R30° orientation relationship is the most stable one at the Al$_2$O$_3$/NiAl(110) interface.
Chapter 8

Oxidation of NiAl(110) at atmospheric pressure

8.1 Introduction

NiAl is an ordered intermetallic material which possesses low density, good oxidation resistance, and metal-like electrical and thermal conductivity. As previously mentioned, owing to their high temperature oxidation resistance, the Ni-Al intermetallics may be used as bond coats in thermal barrier coating (TBC) systems. Therefore, the oxidation of NiAl at high temperature was intensively studied [11, 118, 119, 101, 120, 115, 121, 122, 123, 124] using different techniques. However, to the best of our knowledge, no in situ atmospheric pressure oxidation studies exist on NiAl single crystals, which allow to follow the transition from metastable oxide phases to $\alpha$-$\text{Al}_2\text{O}_3$, offering at the same time the possibility to perform a structural characterization of the oxide and oxide/substrate interface.

We have studied in situ the transition from epitaxial $\gamma$-$\text{Al}_2\text{O}_3$ to $\alpha$-alumina during atmospheric oxidation of a NiAl(110) single crystal. The method of choice is Grazing Incidence X-ray Diffraction (GIXRD) which has proved to be a very useful non-destructive technique that can be used to investigate oxidation processes in situ. Working at grazing angles ensures the required surface sensitivity, since it is the oxide and the oxide/substrate interface we are interested in. In contrast to other surface science techniques, GIXRD does not have limitations concerning the insulating character of the material under investigation and does not require ultra-high vacuum environment. Additional structural information were obtained from cross-section Transmission Electron Microscopy (TEM) images. The cross-sectional TEM specimens were prepared [116] after the in situ diffraction experiments. The TEM measurements were performed$^1$ using an in-house JEM-ARM

$^1$The TEM measurements have been performed by Amalia Catanoiu-Soare and Gunther Richter.
1250 microscope operated at an accelerating voltage of 1250 kV.

This chapter is organized as follows: the experimental set-up for the GIXRD measurements is presented in Section 8.2, followed in Section 8.3.1 by the \textit{ex situ} x-ray diffraction characterization of the preoxidized \(\gamma\)-\(\text{Al}_2\text{O}_3/\text{NiAl}(110)\) system. Section 8.3.2 comprises the \textit{in situ} experimental observation on the transformation of epitaxial \(\gamma\)-\(\text{Al}_2\text{O}_3\) layer to the stable \(\alpha\)-\(\text{Al}_2\text{O}_3\) during high temperature atmospheric pressure oxidation. The \textit{ex situ} x-ray diffraction and TEM observations on the \(\alpha\)-\(\text{Al}_2\text{O}_3/\text{NiAl}(110)\) system are presented in Section 8.4. The chapter concludes with a summary of the experimental findings.

### 8.2 Experimental details

The experiments were performed using a nominally Ni\(_{50}\)Al\(_{50}\) single crystal grown by the floating-zone technique \cite{125}. The sample was cut and polished in (110) orientation better than 0.1\(^\circ\). The surface was cleaned by sputter-annealing cycles in UHV until the surface contaminants were removed. Prior to the \textit{in situ} experiments, the sample was oxidized at 870\(^\circ\)C and at a pure oxygen pressure of 1 bar for 10 minutes. The oxide layer was first characterized by performing \textit{ex situ} GIXRD measurements. The first set of data was taken using a six circle diffractometer installed at a laboratory rotating anode x-ray source. The measurements were done in a horizontal sample geometry (with its surface normal vertical) using Mo K\(\alpha\) radiation with a wavelength of 0.70926 Å. A graphite monochromator was used allowing a separation of the K\(\alpha\) and K\(\beta\) lines. The angular acceptance of the detector was 0.4\(^\circ\) normal to the surface and 0.4\(^\circ\) parallel to the surface. Structural information of the oxide layer were obtained from the out-of-plane diffraction data. In addition, some in-plane data were taken in order to obtain additional information regarding the orientation relationship between the oxide and the underlying substrate.

For the examination of the oxide phase transformations during further oxidation, \textit{in situ} in-plane measurements\(^2\) were carried out using synchrotron radiation at the MPI-MF surface diffraction beamline at ANKA, Karlsruhe \cite{61}. The wavelength was chosen to be 1.1808 Å (10.5 keV). The sample was mounted in vertical scattering geometry inside the Anton Paar HTK 1200N high temperature furnace. The temperature was measured using a Pt 10\% RhPt thermocouple. The experimental set-up used during the beamtime is illustrated in Fig. 8.1. The oxidation experiments were performed in air at temperatures ranging from 800 to 1200\(^\circ\)C. Due to the limited width of the furnace’s window it was not possible to perform \textit{in situ} out-of-plane measurements. Therefore, after the oxidation at 1200\(^\circ\)C, the out-of-plane structure of the oxide layer was investigated performing \textit{ex situ} measurements.

\(^2\)The diffraction data presented in this chapter were obtained during the ANKA3 beamtime.
8.3 Results and discussions

8.3.1 Characterization of the preoxidized NiAl(110)

Prior to the in situ GIXRD measurements, the NiAl(110) crystal has been oxidized for 10 minutes at 870°C and 1 bar oxygen and a layer of epitaxial γ-Al₂O₃ oxide. Ex situ x-ray diffraction investigations were performed to probe the crystallographic structure of the oxide using the laboratory set-up described above. The in-plane and the out-of-plane structure of the oxide layer will be described in the following.

A. In-plane structure of γ-Al₂O₃

In order to establish the orientation of the γ-Al₂O₃ layer with respect to the substrate, in-plane rocking scans over a wide angular range (in which the value of the in-plane momentum transfer, Q, is kept constant) and in-plane radial scans are necessary. The hexagonal unit cell—shown in Fig. 7.9—was chosen to describe the symmetry of the (111) planes of the γ-Al₂O₃ bulk unit cell; the intrinsic hexagonal lattice constants are \(a=b=5.531\ \text{Å},\ c=13.55\ \text{Å}\) and \(\alpha=\beta=90°,\ \gamma=120°\). It should be noted that all the γ-Al₂O₃ reflections were indexed using the hexagonal unit cell, whereas the substrate reflections are labeled according to the bulk unit cell.
Figure 8.2: (a) Diffracted intensity as a function of the in-plane rotation angle, θ, with the scattering angle fixed on the (0, 0, 2) reflection of NiAl. (b) Radial in-plane scan through NiAl (1, 1, 0) reflection, (1, 1, 0), and (2, 0, 2) reflections of γ-Al₂O₃. (c) In-plane view of the reciprocal in-plane unit cell of the substrate (open black symbols) and the relaxed γ-Al₂O₃(111) (filled red symbols) having the R30° orientation relationship.

Fig. 8.2(a) shows the diffracted intensity as a function of the azimuthal sample angle, θ (rotation of the sample around the surface normal). The scan was performed with the incident angle equal to the critical angle for total external reflection of the oxide layer, i.e., $\alpha_i = 0.26^\circ$. The in-plane momentum transfer was kept at $Q = 4.3764 \text{ Å}^{-1}$, corresponding to (0, 0, 2) reflection of NiAl. In between the (0, 0, 2) and (0, 0, 2) reflections of NiAl, three additional peaks can be observed. These are compatible with the six-fold symmetry of the (111) planes in γ-Al₂O₃ and were identified to be the γ (2, 2, 0)-type reflections (or the (4, 4, 0) reflection using the bulk γ-Al₂O₃ coordinates).

A radial scan through the oxide peaks [not shown here] revealed that their position is slightly shifted to a higher Q-value, i.e., 4.544 Å$^{-1}$, as compared to that of the (0, 0, 2) reflection of NiAl, indicating that the oxide lattice is relaxed with respect to the underlying substrate. However, the oxide peaks were found to be rather broad in the radial direction.
8.3 Results and discussions

Figure 8.3: (a) L-scans in different reciprocal lattice directions normal to the surface. (b) Reciprocal (H,0,L) plane of γ-Al2O3.

which explains why there is a contribution even in the rocking scan performed with Q=4.3764 Å⁻¹. Along the [110] direction of NiAl, in addition to the substrate (1,1,0) peak, the γ(2,2,0) and γ(1,1,0) reflections of the γ-Al2O3 were found. This is shown in Fig. 8.2(b). The scan was performed at an incident angle equal with the critical angle of the oxide in order to enhance the signal from the γ-Al2O3 layer. The presence of the γ(1,1,0) reflection is an additional proof that the oxide layer consists of γ-Al2O3, since for α-Al2O3 this reflection does not appear. Fig. 8.2(c) shows a sketch of the reciprocal in-plane unit cell of the substrate (open black symbols) and the relaxed γ-Al2O3(111) (filled red symbols) having the R30° orientation relationship. The aforementioned experimental observations give direct evidence for the R30° orientation relationship³ which can be summarized as follows: NiAl(110)bcc∥γ-Al2O3(111)fcc and [211]fcc γ-Al2O3∥[001]bcc NiAl.

B. Out-of-plane structure of γ-Al2O3

The measurements described in the previous section probed only the in-plane structure of the oxide layer with respect to the substrate. In order to complete the structural characterization, additional information are needed. These are obtained performing out-of-plane measurements along the reciprocal lattice directions, providing an additional momentum transfer perpendicular to the surface, Q⊥ [52].

Fig. 8.3(a) shows three out-of-plane scans as a function of the γ-Al2O3 reciprocal lattice coordinate, L, where L=1 corresponds to the reciprocal lattice unit of the oxide |c'| = 2π/c=0.4638 Å⁻¹. The reflections were indexed using the coordinates of the hexagonal

³A description of the possible orientation relationships at fcc(111)/bcc(110) interface was offered in Chapter 7.
8.3.2 In situ oxidation at atmospheric pressures

After the ex situ characterization, the sample was introduced into the Anton Paar furnace described previously and In situ measurements were performed at the MPI-MF beamline at ANKA, Karlsruhe using a photon energy of 10.5 keV to study the phase transition and oxidation behavior was investigated during oxidation in air at temperatures ranging from 800–1200°C. The sample was first heated at 800°C with a heating rate of 20°C per minute. As can be seen in Fig. 8.4, the temperature was then raised in five steps to 1025°C. During each step, rocking scans were performed on the γ(2,2,0) reflection to study the evolution of the mosaic distribution in the oxide layer. A continuous increase in the FWHM (Full Width of Half Maximum) of the γ(2,2,0) peak was observed, which is a precursor for the shearing of the oxygen ion planes during the fcc-hcp-like martensitic phase transformation from γ-Al₂O₃ to α-Al₂O₃. In addition, a radial scan in the (110) direction of the substrate is shown in Fig. 8.5(a) for T=1025°C, which indicates the formation of a new metastable phase, δ-Al₂O₃. One can observe the appearance of a new peak close to the γ(2,2,0) reflection: in addition to the NiAl (1,0,0) and the γ(2,2,0)
Figure 8.5: (a) Radial in-plane scan in the (1, 1, 0) direction of the substrate during oxidation at 1025°C. (b) Radial scan through the (2, 2, 0) and (3, 0, 3) reflection of γ-Al2O3 and α-Al2O3, respectively. (c) Diffracted intensity as a function of the in-plane rotation angle, θ, with the scattering angle fixed on the (3, 0, 3) reflection of α-Al2O3 during oxidation at 1025°C (after the sample was cooled down to room temperature and heated up again).

After eight hours at 1025°C, the sample was cooled down to room temperature and heated up again at 1025°C. After another hour at 1025°C, a high resolution radial scan through the γ(2, 2, 0) reflection revealed the presence of the δ(4, 0, 12) and α(3, 0, 3) peaks, as seen in Fig. 8.5(b). The fitting was done using a Gaussian lineshape for each of the peaks: red peak corresponds to the γ (2, 2, 0) reflection, the magenta and blue peaks correspond to the δ(4, 0, 12) and α(3, 0, 3) reflections, respectively. A rocking scan performed with the scattering angle fixed on the α(3, 0, 3) reflection is plotted in the Fig. 8.5(c). The sharp peak superimposed on a strong background indicates the coexistence of polycrystalline and epitaxial α-Al2O3, as will be evidenced further below. The fitting was done using a Lorentzian lineshape with a constant background. The sharp component is due to the epitaxial α-Al2O3, while the broad component is due to the contribution of the polycrystalline alumina (Debye-Scherrer ring).

The relative orientation relationship between the epitaxial α-alumina and the un-
derlying substrate was determined to be NiAl(110) $\parallel \alpha$-Al$_2$O$_3$ (0001) and $[\overline{1}1\overline{0}]$ NiAl $\parallel [2130] \alpha$-Al$_2$O$_3$. It should be noted that during the transformation of the epitaxial $\gamma$- to epitaxial $\alpha$-Al$_2$O$_3$ the orientation of the oxygen sublattice with respect to the substrate remains unchanged. It is the originally fcc oxygen arrangement in $\gamma$-alumina (ABCABC layer sequence) that is converted into the hcp stacking ABAB by shearing of the O$_2^-$ ion planes and cation rearrangement. The (111) $\gamma$-Al$_2$O$_3$ plane becomes the (0001) plane of corundum. A top view of the real space orientation of the oxygen sublattice (blue spheres) in the epitaxial $\gamma$ and $\alpha$-alumina with respect to the substrate unit cell is shown in Fig. 8.6[right]. The green and the orange spheres represent the Ni and the Al inside the substrate unit cell, respectively. The sketch in Fig. 8.6[left] represents the corresponding in-plane reciprocal space of NiAl(110) (black open circles), $\gamma$-Al$_2$O$_3$ (111) (red filled circles) and $\alpha$-Al$_2$O$_3$ (0001) (blue circles).

Fig. 8.7 shows rocking scans with the scattering angle fixed on the (3, 0, 3, 0) reflection of $\alpha$-Al$_2$O$_3$ performed during the oxidation at 1100$^\circ$C. The incident angle was fixed to $\alpha_i=0.4^\circ$ and the exit angle equal to $\alpha_f=0.56^\circ$, $\alpha_f=2^\circ$ and $\alpha_f=4^\circ$, respectively. The presence of a peak in the rocking scan even at large exit angles—the CTR signal—is an indication of a smooth oxide layer.

At 1100$^\circ$C the radial scans revealed the presence of polycrystalline $\delta$- and $\alpha$-Al$_2$O$_3$, as can be seen in Fig. 8.8(a). After two hours at this temperature, the transformation to $\alpha$-Al$_2$O$_3$ was complete: no $\delta$-Al$_2$O$_3$ reflections were present. The first scan (magenta line) was performed immediately after heating at 1100$^\circ$C, whereas the other scan (blue line) was recorded two hours later. At 1200$^\circ$C the oxide scale was found to consist of solely
8.3 Results and discussions

Figure 8.7: Diffracted intensity as a function of the in-plane rotation angle, $\theta$, with the scattering angle fixed on the $(3, 0, 3, 0)$ reflection of $\alpha$-$\text{Al}_2\text{O}_3$ during oxidation at 1100°C.

$\alpha$-$\text{Al}_2\text{O}_3$. Fig. 8.8(b) shows two radial in-plane scans performed through the $\alpha(3, 0, 3, 0)$ reflection (red line) and in an arbitrary direction (black line), respectively. For a better comparison the intensity of the black scan was multiplied by a factor of two. These scans were recorded during oxidation at 1200°C with the incident angle fixed to $\alpha_i=0.4^\circ$. All the peaks were identified to belong to $\alpha$-$\text{Al}_2\text{O}_3$. It can be easily observed, that the $\alpha(3, 0, 3, 0)$ reflection is much weaker when the scan is performed in an arbitrary direction, in which all the diffracted intensity is due to polycrystalline alumina. Since the epitaxial $\alpha$-$\text{Al}_2\text{O}_3$ contributes to the diffracted intensity only when the scan is performed in the $[110]_{\text{NiAl}}$ direction, this is a clear indication that the epitaxial $\alpha$-$\text{Al}_2\text{O}_3$ is preserved even at 1200°C.

After five hours of oxidation at 1200°C, the sample was cooled down to room temperature with 20°C per minute and the same in-plane measurements were repeated. From the room temperature in-plane XRD measurements, $d$-spacings of several $\alpha$-$\text{Al}_2\text{O}_3$ planes

![Figure 8.8: (a) Radial in-plane scans during oxidation at 1100°C. (b) Radial in-plane scans through $\alpha$-$\text{Al}_2\text{O}_3$ (3,0,3,0) reflection (black line) and in a non high symmetry direction (red line) during oxidation at 1200°C.]
Table 8.1: The d-spacing from the diffraction data (d), strain free d-spacing (d$_0$) and the calculated strain values for α-Al$_2$O$_3$. The strain free lattice constants were considered to be a$_0$=4.7589 Å and c$_0$=12.991 Å [87]. The thermal expansion coefficient of α-Al$_2$O$_3$ at 1200°C is α=10.2×10$^{-6}$ K$^{-1}$ [126].

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Room temperature</th>
<th>1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d^{RT}$ (Å)</td>
<td>$d_0$ (Å)</td>
</tr>
<tr>
<td>(3, 0, 3, 0)$_{epi}$</td>
<td>1.366</td>
<td>1.373</td>
</tr>
<tr>
<td>(1, 1, 2, 0)$_{poly}$</td>
<td>2.378</td>
<td>2.379</td>
</tr>
</tbody>
</table>

were evaluated in order to get information about the in-plane strain in the oxide scale. The epitaxial α-Al$_2$O$_3$ is under compressive stress, due to the difference in the thermal expansion coefficients of the oxide and the substrate. However, there is a negligible value of the in-plane strain in the polycrystalline oxide [see Table 8.1]. The low value of strain in the polycrystalline alumina can be attributed to the similar thermal expansion coefficient of the polycrystalline and epitaxial alumina. In order to estimate the growth strains in the oxide scale, the d-spacings for several alumina lattice planes were calculated from the data measured at 1200°C. The thermal expansion coefficient of alumina at the above mentioned temperature is α=10.2×10$^{-6}$ K$^{-1}$ [126]. The growth strain was found to be negligible, both in the epitaxial and in the polycrystalline α-Al$_2$O$_3$ [see Table 8.1]. This is in agreement with previous studies, reporting an initial tensile stress state which declined to zero as soon as the transformation of metastable to α-Al$_2$O$_3$ was complete [11, 12].

8.3.3 Ex situ measurements after oxidation at 1200°C

A. Grazing incidence x-ray diffraction measurements

Out-of-plane structure of α-Al$_2$O$_3$ The out-of-plane structure of α-Al$_2$O$_3$ was probed by measuring the diffracted intensity along nine different rods with the laboratory set-up described before. Fig. 8.9(a) shows the diffracted intensity along the (1̅12L), (1̅01L) and (202L) reciprocal lattice directions as a function of the reciprocal lattice coordinate, L. The reflections were indexed using the α-Al$_2$O$_3$ coordinates. The lattice parameters of α-Al$_2$O$_3$ unit cell are a=b=4.7142 Å and c=12.93 Å, so that L corresponds to the reciprocal lattice unit |c$^*$| = 2π/c=0.4859 Å$^{-1}$.

In Fig. 8.9(b) the fcc-like (01̅10)/(0001) and hcp-like (11̅20)/(0001) reciprocal lattice planes are shown. The fcc-like reciprocal plane is due to the stacking of the missing Al$^{3+}$ ions in the corundum structure. Therefore, similar considerations as for the (H0L) plane of γ-Al$_2$O$_3$ hold [see Fig. 8.3(b) in the section 8.3.1.B]. As for the of γ-Al$_2$O$_3$, twin domains...
8.3 Results and discussions

Figure 8.9: (a) L-scans as a function of the relative coordinate \( L \) in different reciprocal lattice directions normal to the surface. (b) The (0\( \bar{1} \)10)/(0001) (fcc-like) and (11\( \bar{2} \)0)/(0001) (hcp-like) reciprocal planes of \( \alpha \)-Al\(_2\)O\(_3\).

are also present, which can be deduced by the presence of reflections with \( L = 4, 10 \) and \( L = 2, 8 \) in the (0\( \bar{1} \)1\( L \)) and (0\( \bar{2} \)2\( L \)) directions, respectively. Additional peaks appear at non-integer \( L \) values, which are due to the intersection of the \( L \)-scan with Debye-Scherrer rings of polycrystalline alumina.

B. Transmission electron microscopy characterization

To confirm and complete the diffraction data concerning the epitaxial \( \alpha \)-Al\(_2\)O\(_3\) layer, cross-section transmission electron microscopy (TEM) images were recorded for the oxide/substrate interface. Both high resolution (HR-) and conventional (CC-) TEM was performed. Fig. 8.10(a) shows a conventional cross-section transmission microscopy image of \( \alpha \)-Al\(_2\)O\(_3\)(0001) / NiAl(110) system, which directly reveals a well-defined interface between the substrate and the epitaxial oxide layer, whereas small voids could be seen at the epitaxial/polycrystalline alumina interface. In all the TEM specimens which were analyzed, the epitaxial oxide formed a continuous layer all along the interface, having an average thickness of about 150 nm. An atomic view on the epitaxial alumina/substrate interface can be seen in the HR-TEM image in Fig. 8.10(b). The interface is smooth, in agreement with the observed CTR signal [see Fig. 8.7]. The epitaxial relationship determined from the Fourier transformation of the HR-TEM images agrees well with the GIXRD findings. In Fig. 8.11 the atomistic model of the \( \alpha \)-Al\(_2\)O\(_3\)(0001)/NiAl(110) interface viewed along the [10\( \bar{1} \)0] direction of \( \alpha \)-Al\(_2\)O\(_3\) is shown. The small red spheres represent Al ions in the oxide, while the oxygen ions are colored in dark blue. The green and the red spheres represent Ni and Al atoms inside the substrate, respectively.
8.4 Summary

In conclusion, we have performed grazing incidence x-ray diffraction measurements to study the oxidation of NiAl(110). The oxidation at 870°C and 1 bar O\textsubscript{2} leads to the formation of a well-ordered \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} epitaxial layer. The orientation relationship of the oxide layer with respect to the underlying substrate has been determined from the in-plane diffraction measurements and it corresponds to the R30° orientation relationship: NiAl(110\textsubscript{bcc} \parallel \gamma\text{-Al}_2\text{O}_3 (111\text{fcc} and [2\overline{1}\overline{1}]\text{fcc} \gamma\text{-Al}_2\text{O}_3 \parallel [001]\text{bcc} NiAl. Out-of-plane structural characterization of the \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} layer indicate the formation of twin domains, which occur where the \(ABC\) sequence of the oxygen layers is reversed to \(CBA\).

The stability of the \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} epitaxial layer and its transition to \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} phase was
8.4 Summary

Figure 8.11: Atomistic model of the $\alpha$-Al$_2$O$_3$(001)/ NiAl(110) interface viewed along the [1010] direction of $\alpha$-Al$_2$O$_3$.

Further investigated by performing in situ GIXRD measurements during oxidation in air at different temperatures up to 1200°C. The oxide transformation sequence was found to be $\gamma$- $\rightarrow$ $\delta$- $\rightarrow$ $\alpha$-Al$_2$O$_3$. No $\theta$-Al$_2$O$_3$ was formed at any stage of the oxidation, in contrast to other experimental observations: Heuer et al. [11] have reported $\theta$-Al$_2$O$_3$ to be the first oxide phase to form by oxidation of NiAl(110) at 1100°C, which gradually transformed to the thermodynamically stable $\alpha$-Al$_2$O$_3$. We argue that the formation of different alumina polymorphs on the same orientation of NiAl single crystals is due to the different oxidation conditions during the two experiments: in the study by Heuer et al. [11], the NiAl crystal was heated directly to 1100°C, whereas in the present study the temperature was raised in six steps to 1100°C. It is known that $\delta$-Al$_2$O$_3$ is less stable than $\theta$-Al$_2$O$_3$, therefore the former is expected to form at lower oxidation temperatures. In addition, the formation of $\delta$-Al$_2$O$_3$ might be promoted by the preexisting $\gamma$-Al$_2$O$_3$ due to the structural similarities between the two phases.

At temperatures around 1000°C there is a coexistence of epitaxial $\gamma$- and polycrystalline $\delta$-Al$_2$O$_3$. The observed reflections of $\delta$-Al$_2$O$_3$ correspond to those of the tetragonal structure reported by Lippens et al. [84]. $\alpha$-alumina starts to form at 1025°C and only at 1100°C the $\delta$- $\rightarrow$ $\alpha$-Al$_2$O$_3$ transformation was complete.

At 1200°C the oxide scale was observed to consist of both polycrystalline and epitaxial $\alpha$-Al$_2$O$_3$. The relative orientation relationship between the epitaxial $\alpha$-alumina and the underlying substrate was determined to be NiAl(110) $\parallel$ $\alpha$-Al$_2$O$_3$ (0001) and [110] NiAl $\parallel$ [2130] $\alpha$-Al$_2$O$_3$. A recent ab initio thermodynamics study [10] on the $\alpha$-Al$_2$O$_3$(0001) /
NiAl(110) interface stability reports the experimentally observed orientation relationship as the most stable one for this interface. Several other configurations have been tested which lead to much higher interfacial mismatch, and therefore much larger interfacial energies as compared to the aforementioned orientation.

The cross-section TEM observations confirmed the presence of a continuous layer of epitaxial $\alpha$-Al$_2$O$_3$ having a thickness of about 150 nm. The TEM images revealed also a well-defined interface between the substrate and the epitaxial layer. Therefore, it can be concluded that the initial $\gamma$-Al$_2$O$_3$ layer transforms directly into the epitaxial $\alpha$-Al$_2$O$_3$. This corresponds to a fcc–hcp transformation of the oxygen ion sublattice. It is important to underline that during this transformation the orientation of the oxygen sublattice with respect to the substrate remains unchanged. Its crystallographic nature resembles that of a martensitic transformation and it proceeds by shearing of the oxygen ion planes (the stacking is changed from $ABCABC$ in $\gamma$-Al$_2$O$_3$ to $ABAB$ in $\alpha$-Al$_2$O$_3$), as well as by the rearrangement of the cations in the lattice.

From the room temperature in-plane XRD measurements, the residual in-plane strain in the oxide scale was estimated. The epitaxial $\alpha$-Al$_2$O$_3$ was found to be under compressive stress, due to the difference in the thermal expansion coefficients of the oxide and the substrate. A negligible value of the residual in-plane strain in the polycrystalline alumina was found which is explained similar thermal expansion coefficients of the polycrystalline and epitaxial alumina. The growth strain was found to be negligible, both in the epitaxial and in the polycrystalline $\alpha$-Al$_2$O$_3$, in agreement with previous studies, reporting an initial tensile stress state which declined to zero as soon as the transformation of metastable aluminas to $\alpha$-Al$_2$O$_3$ was complete [11, 12].
Chapter 9

Summary

In this work, the transition from ultra-thin oxide layers to bulk oxides during thermally controlled oxidation of CoGa(100) and NiAl(110) has been studied as a function of temperature and the oxygen pressure. In particular, the structure, morphology and thickness of the oxide layer, epitaxial orientation relationship, domain structure, and changes in the substrate due to selective oxidation, were thoroughly investigated. The main experimental methods employed in this work were surface x-ray diffraction (SXRD) and high resolution core level spectroscopy (HRCLS). Prior to the synchrotron experiments, the cleanliness and structure of the samples surface were monitored by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The SXRD and HRCLS measurements have been performed making use of the brilliant synchrotron radiation at various facilities, i.e., Angströmquelle Karlsruhe (Germany), European Synchrotron Radiation Facility (France) and Max-LAB (Sweden). Complementary information has been obtained by means of transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements. Moreover, the results of first-principles thermodynamics on the stability of surface oxides were used to complement the experimental data.

Oxidation of CoGa(100)

The formation of a well-ordered ultra-thin surface gallium oxide layer was previously observed after exposing a CoGa(100) surface at relatively low temperatures and oxygen pressures. LEED measurements show a \((2\times1)\) reconstruction in two domains perpendicular on each other. In this work, an atomic level understanding of the structure of this surface gallium oxide has been achieved based on the combined use of experimen-

---

1The TEM measurements have been performed by A. Catanoiu, Y. Jin-Phillipp and G. Richter.
2The AFM measurements have been performed by E. Barrena and X. Zhang.
3The DFT calculations have been performed by G. Kresse and M. Marsman.
tal (SXRD, HRCLS) and theoretical methods (DFT-based calculations). The resulting structural model contains the basic building block of bulk $\beta$-Ga$_2$O$_3$, although deviations from the bulk phase stoichiometry are observed. The oxide film consists of an oxygen ion double layer with two Ga ions located in truncated octahedral and tetrahedral sites of the fcc oxygen ion sublattice. At the interface, Ga ions occupy sites of the corresponding stacking sequence of the bulk $\beta$-Ga$_2$O$_3$. The two oxygen interfacial atoms share half of their bonds with the strongly buckled Ga substrate atoms, recovering the formal oxidation state of Ga$^{3+}$ in the oxide film. The thickness of the surface gallium oxide film was determined to be 4.5 Å. Additional information have been obtained by means of HRCLS measurements. The decomposition of the Ga 3$d$ spectrum revealed three oxygen-induced components, whereas two components split by 0.6 eV could be identified in the O 1$s$ spectrum. The calculated Ga 3$d$ and O 1$s$ core-level shifts (including final state effects) agree well with the experimental core-level spectra.

The stability diagram of gallium oxide on the CoGa(100) surface was mapped out by means of in situ SXRD measurements. Both a surface oxide and the bulk $\beta$-Ga$_2$O$_3$ phase were identified, even though, according to thermodynamical considerations, only the bulk $\beta$-Ga$_2$O$_3$ is predicted to form throughout the investigated ($p$-$T$) range. The surface oxide forms under metastable equilibrium conditions. The surface oxide structure was preserved at room temperature even at pressures as high as 1 bar O$_2$, maintaining its high degree of crystallinity. The bulk oxide growth was found to be limited by kinetics, which hinder its formation for temperatures lower than 350°C (within the experimentally accessed time scale). At higher temperatures, three-dimensional bulk Ga$_2$O$_3$ islands grows epitaxially on CoGa(100), provided that enough oxygen is supplied to the system.

HRCLS measurements have been performed after oxidation at temperatures up to 750°C and pressures between $10^{-8}$ and $5\times10^{-5}$ mbar O$_2$. An additional higher binding energy component has been identified for both the Ga 3$d$ and O 1$s$ core-level spectra after oxidation at 750°C. This could be an indication of a CoGa$_2$O$_4$ spinel formation.

SXRD measurements showed that at temperatures higher than 750°C, the formation of the bulk gallium oxide is accompanied by substrate faceting. The facets and the substrate join at a 26° angle, as determined from the SXRD measurements, corresponding to (1, 0, 2)-type of planes. Ex situ AFM measurements indicated a similar, i.e., faceted, morphology of the oxide surface.

In conclusion, the multi-technique approach adopted in this work is very well suited for investigating the structure, morphology and stability of oxide layers grown on different metallic alloys. This study shows that the thickness and structural perfection of the oxide layers on alloys can be tailored by the appropriate choice of oxygen pressure and
temperature, which is of crucial importance for all applications involving ultrathin oxide films.

**Oxidation of NiAl(110)**

**Medium pressure oxidation of NiAl(110)**

Within this project, SXRD measurements have been employed for structural characterization and *in situ* evolution of the aluminium oxide/NiAl(110) system during oxidation at different temperatures and oxygen pressures ranging from $5 \times 10^{-6}$ up to 10 mbar O$_2$.

An ultra-thin aluminum oxide layer was grown by thermal oxidation using the well-established recipe: oxidation at 270$^\circ$C with $5 \times 10^{-6}$ mbar O$_2$ for 15 minutes followed by annealing at 800$^\circ$C for 5 minutes [7]. We have performed SXRD measurements in order to probe the ultra-thin aluminium oxide/NiAl(110) structure. The experimental in-plane structure factors are consistent with the data published by Stierle *et al.* [7]. A comparison between our experimental data and the model proposed by Kresse *et al.* [8] was made. The experimental in-plane structure factors were reproduced with less accuracy by this model, as compared to the model proposed by Stierle *et al.* [7]. Although reasonable agreement was found on the surface rods (sensitive to the oxide structure), the poor agreement on the crystal truncation rods proved that the DFT-based model lacks some structural features and can not accurately describe the oxide/alloy interface.

Structural refinement of the oxide/alloy interface was performed and two different models were found to reproduce the experimental data. The characteristic structural feature of the first model is the presence of point defects (Al anti-site atoms) in the topmost substrate layer. It is consistent with the model previously proposed by Stierle *et al.* [9]. The second model assumes a perfect bulk stoichiometry and $\mathbf{z}$-displacements of the atoms in the first three substrate layers. The unambiguous discrimination between these two models is still a critical issue. We expect that anomalous scattering measurements at the K adsorption edge of Ni will provide the information needed to single out the correct model.

The transition of the ultra-thin aluminium oxide to bulk Al$_2$O$_3$ was followed *in situ* at 350$^\circ$C. The ultra-thin oxide was found to be stable up to 0.01 mbar O$_2$. The sample was subsequently annealed at 800$^\circ$C in order for the newly formed oxide to crystallize. The coexistence of surface oxide and epitaxial $\gamma$-Al$_2$O$_3$ oxide islands showing the Kurdjumov-Sachs orientation was observed. Structural refinement of the oxide/alloy interface was performed based on the CTR data. The main structural feature of the resulting interface model is the presence of Ni anti-site atoms which occur in the first two substrate layers.
with 69% and 58% probability, respectively. The enrichment of Ni at the interface appears as a consequence of Al consumption by selective oxidation. For an aluminium oxide layer being in contact with a NiAl(110) alloy having a composition in the Ni-rich region, the formation of Ni anti-site atoms at the interface has been predicted in a recent ab initio thermodynamics study [10], in agreement with our experimental observations.

After oxidation of the NiAl(110) substrate at 800°C and 10 mbar O₂, γ-Al₂O₃ oxide islands formed showing the Kurdjumov-Sachs, Nishiyama-Wassermann and R30° in-plane orientation. In addition, the presence of polycrystalline δ-Al₂O₃ was identified. Cross-section transmission electron microscopy images of the aluminium oxide/NiAl(110) interface revealed an oxide layer having an overall thickness of about ~70 nm. The epitaxial γ-Al₂O₃ did not form a continuous layer on top of the substrate. The formation of cavities was identified at the oxide/substrate interface.

In conclusion, our work provides detailed insight into the stability of the ultra-thin aluminium oxide layer on NiAl(110) at different conditions of oxygen pressures and temperatures. We demonstrated that the thickness of the ultrathin aluminum oxide can not be further increased by multiple oxidation cycles and it only exists as a 5 Å thick layer. Further oxidation induces a drastic change in the oxide morphology, which in turn can have important implications on the behavior of model catalysts deposited on the aluminium oxide layer/NiAl(110), since changes in the oxide structure can influence the catalytic behavior of metal particles.

**Atmospheric pressure oxidation of NiAl(110)**

Grazing incidence x-ray diffraction (GIXRD) and TEM measurements were employed to study the atmospheric pressure oxidation of NiAl(110). The oxidation at 870°C and 1 bar O₂ leads to the formation of a well-ordered γ-Al₂O₃ epitaxial layer. The orientation relationship at the oxide/substrate interface has been determined to be NiAl(110)_{bcc} || γ-Al₂O₃ (111)_{fcc} and [21̅1]_{fcc} γ-Al₂O₃ || [001]_{bcc} NiAl, which corresponds to R30° orientation relationship.

The transition from γ- to α-Al₂O₃ was further investigated during oxidation in air at different temperatures up to 1200°C by means in situ GIXRD measurements. The oxide transformation sequence was found to be γ- → δ- → α-Al₂O₃. α-alumina starts to grow at 1025°C. At 1200°C no metastable aluminas were present and the oxide scale was observed to consist of both polycrystalline and epitaxial α-Al₂O₃. The relative orientation relationship between the epitaxial α-alumina and the underlying substrate was determined to be NiAl(110) || α-Al₂O₃ (0001) and [110] NiAl || [2130] α-Al₂O₃.

From the room temperature in-plane XRD measurements, the residual in-plane strain
in the oxide scale was estimated. The epitaxial $\alpha$-$\text{Al}_2\text{O}_3$ was found to be under compressive stress, due to the difference in the thermal expansion coefficients of the oxide and the substrate. A negligible value of the residual in-plane strain in the polycrystalline alumina was found, which is understood in terms of similar thermal expansion coefficients of the polycrystalline and epitaxial alumina. The growth strain was found to be negligible, both in the epitaxial and in the polycrystalline $\alpha$-$\text{Al}_2\text{O}_3$, in agreement with previous studies reporting an initial tensile stress state which declined to zero as soon as the transformation of metastable to $\alpha$-$\text{Al}_2\text{O}_3$ was complete [11, 12].

Ex situ TEM investigations gave evidence of a continuous layer of epitaxial $\alpha$-alumina having a thickness of about 150 nm. The initial $\gamma$-$\text{Al}_2\text{O}_3$ layer transforms directly into the epitaxial $\alpha$-$\text{Al}_2\text{O}_3$ by a fcc–hcp martensitic-like transformation of the oxygen ion sublattice. However, the orientation of the oxygen sublattice with respect to the substrate remains unchanged during the transformation, that means it is the same as in the $\gamma$-$\text{Al}_2\text{O}_3$ having the R30° orientation. A recent theoretical study [10] has put forward the observed orientation as being the most stable one at the $\alpha$-$\text{Al}_2\text{O}_3$ (0001) / NiAl(110) interface.

We conclude that the orientation of the initial $\gamma$-alumina layer plays a key role in the further growth of epitaxial $\alpha$-$\text{Al}_2\text{O}_3$: it was shown that depending on the oxidation conditions, $\gamma$-$\text{Al}_2\text{O}_3$ having different orientation relationships can be grown on NiAl(110) surface. As described earlier, oxidation of NiAl(110) at 800°C and 10 mbar O$_2$ results in the growth of $\gamma$-$\text{Al}_2\text{O}_3$ showing all three orientation relationships embedded in a polycrystalline $\delta$-$\text{Al}_2\text{O}_3$ oxide. In contrast, a well-ordered $\gamma$-$\text{Al}_2\text{O}_3$ layer was found to form at a slightly higher temperature, 870°C and 1 bar O$_2$.

We argue that the induced growth of an epitaxial $\alpha$-$\text{Al}_2\text{O}_3$ layer could be significant for the practical applications of Ni-Al intermetallics as bond coats in the thermal barrier coating systems. Since the bond coat is polycrystalline, it will be interesting to investigate the growth of epitaxial $\alpha$-alumina on NiAl single crystals having other orientations, i. e., (100) and (111). Pre-oxidizing the bond coat to form large epitaxial oxide grains is expected to lead to a decreased growth rate of the thermally grown oxide ($\alpha$-alumina), since less grain boundaries would be available for ion diffusion. This, in turn, would be beneficial for the lifetime of the aforementioned systems, since it was shown that the failure of thermal barrier coating can be correlated with a critical thickness of the thermally grown oxide [13].
Appendix A

Atomic coordinates of surface gallium oxide model

Table 9.1: Atomic coordinates for the (a) experimental and (b) DFT model of the surface gallium oxide on CoGa(100).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
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(a) Experimental model  (b) DFT model
Appendix B

HRCLS fit parameters

Table 9.2: The fit parameters for the Ga 3d spectrum shown in Fig. 6.13(a).

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<th>Peak</th>
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<th>$\alpha$</th>
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<td>(meV)</td>
<td>(meV)</td>
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Table 9.3: The fit parameters for the O 1s spectrum shown in Fig. 6.13(b).

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<th>$\alpha$</th>
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<td>(meV)</td>
<td>(meV)</td>
<td>(meV)</td>
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# Appendix C

## Acronyms

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<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>ANKA</td>
<td>Ångströmquelle Karlsruhe</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>CLS</td>
<td>Core Level Spectra</td>
</tr>
<tr>
<td>CTR</td>
<td>Crystal Truncation Rod</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>ESRF</td>
<td>European Synchrotron Radiation Facility</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GFWHM</td>
<td>Gaussian Full Width at Half Maximum</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing Incidence X-ray Diffraction</td>
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<td>HRCLS</td>
<td>High Resolution Core Level Spectroscopy</td>
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<tr>
<td>IMPF</td>
<td>Inelastic Mean Free Path</td>
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<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
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<td>LFWHM</td>
<td>Lorentzian Full Width at Half Maximum</td>
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<tr>
<td>MRAM</td>
<td>Magnetic Random Access Memories</td>
</tr>
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<td>RFA</td>
<td>Retarding Field Analyzer</td>
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<td>RT</td>
<td>Room temperature</td>
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<td>SCLS</td>
<td>Surface Core Level Shift</td>
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<tr>
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<td>Surface X-ray Diffraction</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>TBC</td>
<td>Thermal Barrier Coating</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>----------------------------------</td>
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<tr>
<td>TGO</td>
<td>Thermally Grown Oxide</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>UHV</td>
<td>Ultra High Vacuum</td>
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<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
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Bibliography


Acknowledgments


Acknowledgements

A number of people offered me an important support, not only in scientific matters but also in making these years spent in Stuttgart truly exceptional. I would like to take this opportunity to express my sincere gratitude to:

- **Prof. Helmut Dosch** for giving me the opportunity to carry out this work in a scientifically exciting environment and for his constant support throughout the course of this thesis. The friendly and supportive atmosphere inherent to his group contributed essentially to the final outcome of my work.

- My supervisor, **Dr. Andreas Stierle**, for introducing me to the surface x-ray diffraction field, as well as for his patient and continuous guidance at every stage of my research, for important inputs to the present thesis, and for reading and correcting the thesis manuscript.

- **Prof. Manfred Rühle** for his help and support and for having accepted me as member of the Research Training Group "Innere Grenzflächen in kristallinen Materialien", which gave me the opportunity to widen my knowledge in the field of materials science.

- **Prof. Horst Strunk** for his efforts as the main referee.

- **Prof. Helmut Bertagnolli** for being part of the examination committee.

- My colleagues, for participating at the beamtimes and making those days and nights really enjoyable: **Ioan Costina, Nikolai Kasper, Melissa Delheusy** and **Philipp Nolte**. I would also like to acknowledge the help of **Annette Weißhardt** and **Frank Adams**, as well as the technical support offered during the beamtimes by **Ralf Weigel** (ANKA) and **Frank Renner** (ESRF).

- **Edvin Lundgren** for helpful discussions concerning the interpretation of the core-level spectra.
Acknowledgments

- Esther Barrena and Xuena Zhang for the performance of the AFM measurements.

- Amalia Cătănoiu-Soare, Gunther Richter, Yun Jin-Phillipp for the performance of the TEM measurements.

- Georg Kresse and Martijn Marsman for performing the DFT calculations.

- Sebastian Schöder for translating the thesis summary into German.

- János Major for his helpfulness and very useful LaTeX tips.

- All the members of the Department Dosch at the Max-Planck-Institut für Metallforschung in Stuttgart for all the nice moments I experienced next to them in the last years, for creating a really pleasant and stimulating working environment, for the help and advice they offered whenever needed. I would like to thank particularly to Amalia Cătănoiu-Soare, Ioan Costina, Melissa Delheusy, Claus Ellinger, Nikolai Kasper, Ruslan Kurta, Cristian Mocuta, Philipp Nolte, Max Nülle, Ingo Ramsteiner, Alexander Reicho, Sebastian Schöder, Sorin Soare, Alexander Udyansky, Vedran Vonk.

Finally, I want to especially thank my family. No matter how far, they have always been here and have given me affection and support all along the way, instilling in me confidence and a drive for pursuing my PhD. Mulțumesc!

This project has been financially supported by the Max Planck Society, Deutsche Forschungsgemeinschaft (DFG) within the Graduiertenkolleg "Innere Grenzflächen in kristallinen Materialien" (GRK 285) and by the EC/NSF Project HIPERCOAT (GRD2-200-30 211).